

# SOIL SCIENCE

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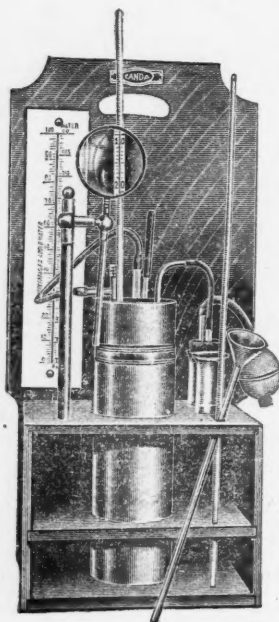
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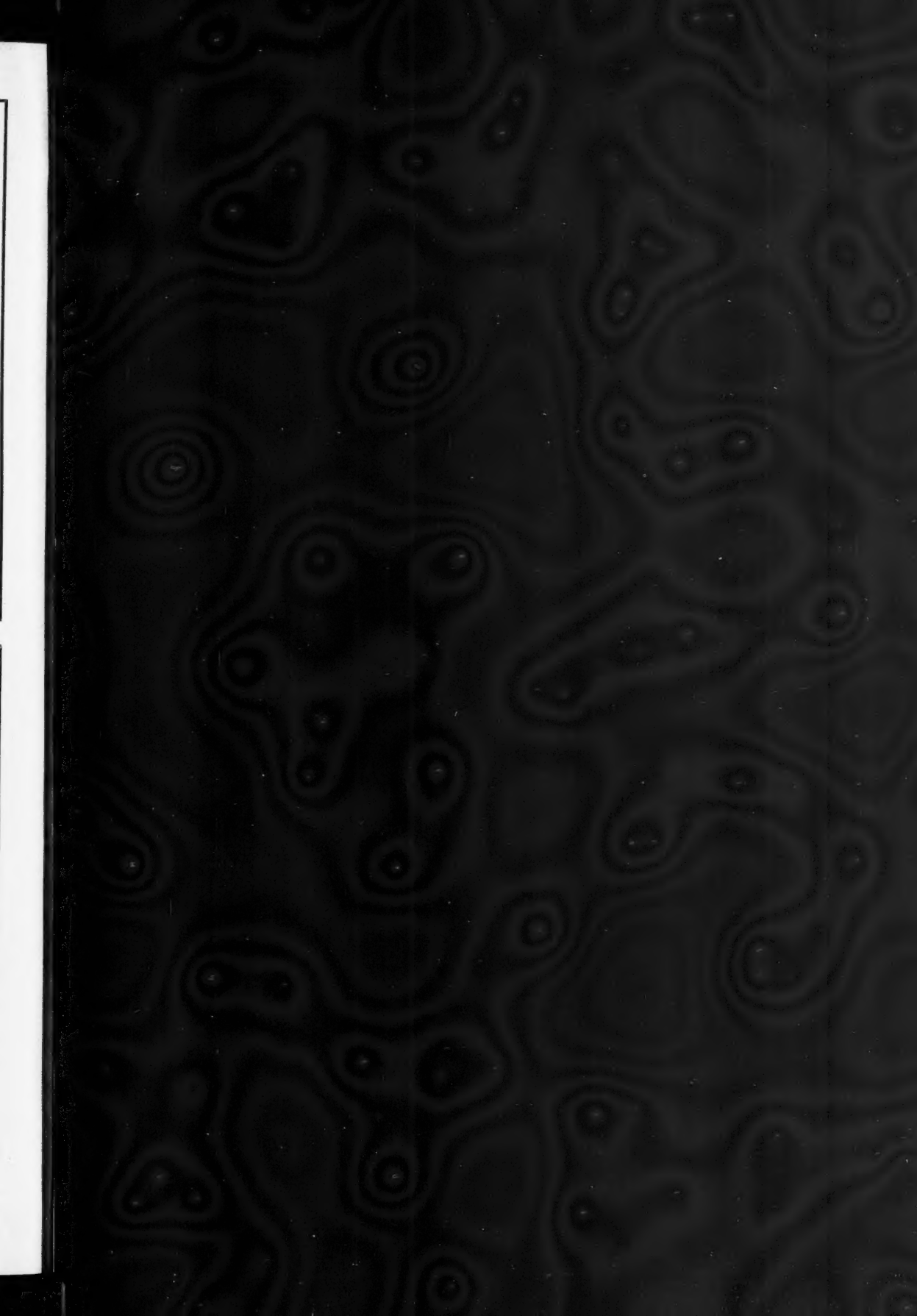
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## THE HUMAN ELEMENT IN THE WORK AT ROTHAMSTED

*Reprinted from the Agricultural Gazette*

It was a happy idea that led Mr. Edwin Grey, field superintendent at the Rothamsted Experimental Station, to write his reminiscences. They cover a period of fifty years. Since his first job at the laboratory, as a boy of thirteen, was in the summer of 1872, he was working there for nearly fifty years in the lifetime of Lawes and Gilbert. Of the men who carried on field operations under the eyes of those two great leaders, we believe he is now the only survivor. His book will serve to keep green the memory of many who helped carry out the work which the founders of the Station planned.

Mr. Grey has produced a very interesting book, none the less so in that it is altogether free from the stiffness and formality of the regular author. He lets his pen run on just as we can imagine his tongue might do, in an easy, unreserved moment, recalling what he has witnessed—the oxen ploughing in the Broadbalk Field, before all the work was done by horses, to give place still later to the tractor—the Harvest Home suppers in the “East Mow”—the Irish laborers—the Christmastide presents—the casuals discussing the merits of “His Majesty’s Hotel” for the winter—the Jubilee festivities—the theatricals in the “Sample House.” He gives us glimpses of a rural life which has altogether vanished, thumbnail sketches of countryside characters which the changes of the last twenty or thirty years have made as obsolete as the very dodo—the old bird scarer who resented Sir John Lawes’ fondness for a rookery, shouting to the birds, “Go back to Rothamsted, you old black devils, and let Jack Lawes look arter yer!”—the man who, as the nights drew in, remarked “That’ll get late proper early tonight, I’ll warrant,”—the boy who entered in his record book, “Through there being no cake, the cows got only half a lot.”

Sir Henry Gilbert is shown as a very human, kindly, if occasionally an irascible old gentleman, losing his temper over misunderstood instructions and being quieted down by Lady Gilbert; or telling the man who thought that the water samples should be brought down in a cart drawn by ‘an experimental donkey,’ “Well, Frank, we’ve already got one or two about here now.” Sir John Lawes too, appears and reappears throughout the volume as the generous squire, as well as the far-seeing man of science. But it is as a record of humbler lives that the book has its greatest charm. It gives us the human side of what countless papers have given the scientific results; and throughout its pages we

are shown the patient toil, the cheerful acceptance of a life of hard work, the patience, the honesty, and good faith of the men, who in their own way had their share in the operations which are inseparably bound up with the name of Rothamsted.

Sir E. J. Russell has written a brief preface, and the book is illustrated with a number of photographs and sketches; but it is the author's straight forward story, revealing quite unconsciously his tact and sympathy, and illuminated by a quiet humor, which is the mainstay of a very delightful volume. The book can be obtained post free for 5s. 9d. from E. Grey, Laboratory Cottages, Harpenden, or from the Secretary, Rothamsted Experimental Station, Harpenden, Herts.

## VARIABILITY OF ALKALI SOIL<sup>1</sup>

W. P. KELLEY<sup>2</sup>

*Citrus Experiment Station, University of California*

Received for publication November 20, 1921

Waynick (5) found that the nitrate content of soil samples drawn from a small area of apparently uniform soil, and especially the amounts of nitrate formed in the samples during a period of four weeks, varied quite widely. Waynick and Sharp (6) found considerable differences in both the nitrogen and the carbon content of soil samples taken at 30-foot intervals from two different areas of apparently uniform soil. McBeth (3) showed that great variability characterizes the distribution of nitrate in the soils of several citrus groves in California. Similar results have been observed by this laboratory.

Those who are familiar with semi-arid regions are quite aware of the sporadic variability of alkali soils. Not infrequently abrupt differences occur in the growth of crops. Good yields may be obtained in a given location, while only a few feet distant neither growth nor germination is possible. The lack of uniformity in the salt content of the soil and other factors (4), some of which will be discussed later, greatly complicate plot experimentation on alkali soils and render it extremely difficult to secure uniform results by the application of a given treatment. As is shown below, the usual method of sampling alkali soil may be quite unreliable.

### EXPERIMENTAL PLOTS

In connection with an alkali reclamation experiment consisting of approximately seven acres, and located on a quarter section of the Kearney Ranch near Fresno, California, a large number of soil samples have been analyzed. The experiment was begun in May 1920, just previous to harvesting that season's barley crop. The soil appeared to be as nearly uniform as could be found anywhere within the entire quarter section. The barley crop of 1920 was a complete failure on the greater portion of the area. On much of it the seed had failed to germinate, although the moisture and other seasonal conditions were quite favorable for growth. There were several small spots within this area, however, on which the barley made slight growth, and on a few spots a reasonably good yield was obtained.

<sup>1</sup> Paper No. 86, University of California, Graduate School of Tropical Agriculture and Citrus Experiment Station, Riverside, California.

<sup>2</sup> Analyses reported were made by S. M. Brown, Assistant in Chemistry, at the Citrus Experiment Station.

The experiment consists of 9 plots 100 feet by 330 feet in size. After making an accurate map showing the barley and weed growth, a line was drawn across the greatest length of each plot, and soil samples were taken on this line, usually at intervals of ten feet. The samples were drawn with a two-inch auger and were taken to represent the first-foot and second-foot depths respectively, and in a considerable number of instances the third-foot and fourth-foot depths also.

Extracts were prepared by shaking a portion of each sample for one hour with distilled water in the ratio of 1:5 and filtering the solutions through Pasteur-Chamberland tubes. The extracts were analyzed by methods previously described (1).

#### RESULTS

As was suggested by the appearance of the barley crop, the analyses show that this soil is distinctly spotted. Every sample from certain spots was substantially different in composition from those taken from other spots. A few of these spots cannot be classified as alkali soil, and certain other spots contain amounts of salts quite different from those of still other spots. The results also show that the distribution of the various salts within spots of apparently uniform soil is extremely variable. The analyses indicate that at least two factors must be taken into consideration in studying the variability of this soil, (a) variation within the several spots and (b), the nature of a given spot as a whole, that is, whether alkali salts are present or absent,<sup>3</sup> and if present, whether the general level of concentration is high or low, etc.

The soluble constituents of those samples which gave a distinct reaction with phenolphthalein were composed principally of sodium salts, but wherever sodium carbonate was absent the amounts of soluble alkaline earths, especially calcium, were substantially greater than in the more highly alkaline spots.

The anions common to alkali soil, the total soluble salts and the pH values of the samples representing the first-foot and second-foot sections of only two plots will be presented here. These plots are fairly representative of the area as a whole. Their analyses are presented in tables 1, 2, 3 and 4.

The data show that this soil varies greatly in composition. In one instance the chloride content of two samples taken ten feet apart differed almost 1000 per cent, and in several other instances differences as great as 100 per cent, or more, were found. The content of the different constituents does not necessarily vary in the same direction. For example, certain samples contained sub-

<sup>3</sup> Because of the complex nature of the variation in this soil the writer does not consider it permissible to apply the usual statistical treatment to the data now at hand. For instance, it was found that the frequency curve obtained by plotting the chlorine of plot 3 bears very little similarity to a theoretical frequency curve. As pointed out by Linhart (2) the usual statistical formula is not applicable to data which give curves widely divergent from the theoretical curve. It should not be inferred, however, that statistical methods cannot be applied to the study of spotted soil. It is not entirely clear to the writer, however, that there is any particular advantage to be derived from a determination of the mean composition of spotted soil.

TABLE 1  
Composition of soil samples, plot 3, first foot\*

SAMPLE NUMBER	1	2	3	4	5	6	7	8	9	10	11	12	13	14
<i>Parts per million</i>														
CO <sub>2</sub> .....	435	375	330	330	285	315	210	330	210	240	120	60	90	90
HCO <sub>3</sub> .....	412	412	336	335	396	412	534	472	472	488	366	427	442	335
Cl.....	913	629	727	140	124	195	629	426	204	167	53	53	35	44
SO <sub>4</sub> .....	474	376	588	70	62		110	129	151	68	39	43	27	29
NO <sub>3</sub> .....	462	201	201	62	62	46	139	15	31	62	62	46	46	62
Total salts.....	4525	3235	3360	1565	1570	1790	2795	2430	1460	1605	990	1050	940	740
pH value.....	9.6	9.6	9.7	9.6	9.6	9.6	9.6	9.6	9.6	9.6	9.0	9.2	9.3	9.2

SAMPLE NUMBER	15	16	17	18	19	20	21	22	23	24	25	26	27	28
<i>Parts per million</i>														
CO <sub>2</sub> .....	195	75	240	225	330	390	270	90	75	105	390	375	450	465
HCO <sub>3</sub> .....	442	320	351	564	366	381	396	351	320	351	457	640	488	442
Cl.....	26	44	44	655	230	362	265	18	35	35	185	133	106	576
SO <sub>4</sub> .....		22	31	88	130	149	103	21	18	27	110	33	266	241
NO <sub>3</sub> .....	31	93	62	124	231	200	77	46	93	62	93	308	201	263
Total salts.....	1005	660	1140	1770	2280	2675	1750	805	765	930	2220	3460	3060	3285
pH value.....	9.6	9.2	9.4	9.5	9.6	9.7	9.6	9.2	9.2	9.2	9.6	9.6	9.6	9.6

\* The distance between samples 13 and 14, 15 and 16, 23 and 24, and 24 and 25, was 20 feet. All other samples were taken 10 feet apart.

TABLE 2  
Composition of soil samples, plot 3, second foot

SAMPLE NUMBER	1	2	3	4	5	6	7	8	9	10	11	12	13	14
<i>Parts per million</i>														
CO <sub>2</sub> .....	120	45	75	15	120	105	120	180	150	150	150	120	105	90
HCO <sub>3</sub> .....	442	549	534	472	320	305	335	351	335	229	366	274	305	320
Cl.....	213	284	364	638	603	825	541	266	222	310	177	124	53	44
SO <sub>4</sub> .....	198	110	130	414	278	387	165	177	119	119	113	68	68	75
NO <sub>3</sub> .....	108	93	108	186	108	62	31	31	0	0	4	0	2	0
Total salts.....	1490	1465	1625	2570	2265	2710	2210	1500	1375	1515	1260	810	750	735
pH value.....	9.6	9.4	9.6	9.2	9.3	9.2	9.4	9.6	9.6	9.6	9.4	9.4	9.6	9.4

SAMPLE NUMBER	15	16	17	18	19	20	21	22	23	24	25	26	27	28
<i>Parts per million</i>														
CO <sub>2</sub> .....	120	30	120	90	75	150	90	45	45	120	210	300	150	150
HCO <sub>3</sub> .....	351	259	503	457	274	335	488	351	274	335	488	488	303	335
Cl.....	35	27	142	248	151	266	426	53	27	80	248	177	284	337
SO <sub>4</sub> .....	66	59	56	108	79	93	179	33	39	44	160	168	183	160
NO <sub>3</sub> .....	0	2	62	155	31	93	31	0	0	0	46	46	31	31
Total salts.....	740	610	1150	1500	1200	1500	1725	620	670	875	1805	2015	1430	2015
pH value.....	9.6	8.6	9.6	9.6	9.0	9.8	9.4	9.0	8.8	9.6	9.7	9.8	9.4	9.6

TABLE 3  
Composition of soil samples, plot 8, first foot\*

SAMPLE NUMBER	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
	Parts per million														
CO <sub>3</sub> .....	210	330	330	330	405	405	420	240	75	0	0	0	0	0	0
HCO <sub>3</sub> .....	381	244	366	412	397	397	488	458	503	275	290	275	198	107	107
Cl.....	894	220	108	354	1133	1070	327	53	18	18	18	18	18	18	18
SO <sub>4</sub> .....	273	117	42	149	537	491	195	66	39	29	26	22	26	18	20
NO <sub>3</sub> .....	90	45	75	90	300	270	150	60	0	0	0	0	0	0	4
Total salts....	3105	1650	1585	2360	5000	4550	2620	1265	750	400	475	350	340	255	250
pH value.....	9.7	9.4	9.7	9.6	9.7	9.8	9.8	9.4	9.2	7.8	7.6	7.6	7.6	7.2	7.4

SAMPLE NUMBER	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
	Parts per million														
CO <sub>3</sub> .....	0	0	0	0	0	0	0	0	0	0	150	210	300	315	435
HCO <sub>3</sub> .....	229	275	275	260	275	229	214	214	229	260	473	564	350	458	412
Cl.....	18	18	18	18	18	18	18	18	18	18	62	45	53	140	168
SO <sub>4</sub> .....	18	21	23	19	22	25	22	20	39	31	54	37	58	132	606
NO <sub>3</sub> .....	4	0	3	0	3	4	0	4	0	20	15	60	60	75	165
Total salts....	280	350	355	365	515	470	540	525	500	550	1120	1050	1365	3275	2050
pH value.....	7.6	8.0	7.8	7.8	8.1	7.6	7.6	7.6	7.8	8.2	9.6	9.6	9.7	9.6	9.8

\* Distance between samples 16 and 17 was 30 feet. All other samples were taken 10 feet apart.

TABLE 4  
Composition of soil samples, plot 8, second foot

SAMPLE NUMBER	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
	Parts per million														
CO <sub>3</sub> .....	15	0	75	120	75	120	285	390	195	60	0	0	0	0	0
HCO <sub>3</sub> .....	199	244	366	244	199	199	214	259	290	305	214	153	153	92	122
Cl.....	798	1283	691	840	363	470	372	204	80	71	18	89	27	53	35
SO <sub>4</sub> .....	258	428	264	313	126	216	160	124	24	31	28	24	33	25	23
NO <sub>3</sub> .....	0	9	16	9	18	46	46	15	5	0	0	2	2	0	0
Total salts....	2090	3000	2090	2085	1280	1850	2055	2050	1000	670	425	400	250	255	255
pH value.....	8.4	...	9.2	9.4	9.4	9.6	9.6	9.6	9.6	9.4	8.0	7.8	7.8	8.0	7.8

SAMPLE NUMBER	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
	Parts per million														
CO <sub>3</sub> .....	0	0	0	0	15	0	0	0	0	30	150	105	180	150	90
HCO <sub>3</sub> .....	153	106	229	199	381	198	153	168	183	305	244	351	274	229	214
Cl.....	44	44	27	62	35	124	35	53	35	53	115	160	363	284	230
SO <sub>4</sub> .....	25	32	31	33	30	41	23	33	18	24	82	103	271	242	140
NO <sub>3</sub> .....	0	0	0	0	4	5	0	0	3	9	46	18	18	31	9
Total salts....	300	300	275	255	225	215	230	220	290	490	1600	1210	1685	1500	715
pH value.....	7.8	7.8	8.0	7.6	8.8	7.6	7.8	7.8	7.6	8.6	9.6	9.6	9.6	9.6	9.0

stantially greater amounts of chloride than of any other ion, while other samples contained greater amounts of normal carbonate, sulphate or nitrate than of chloride.

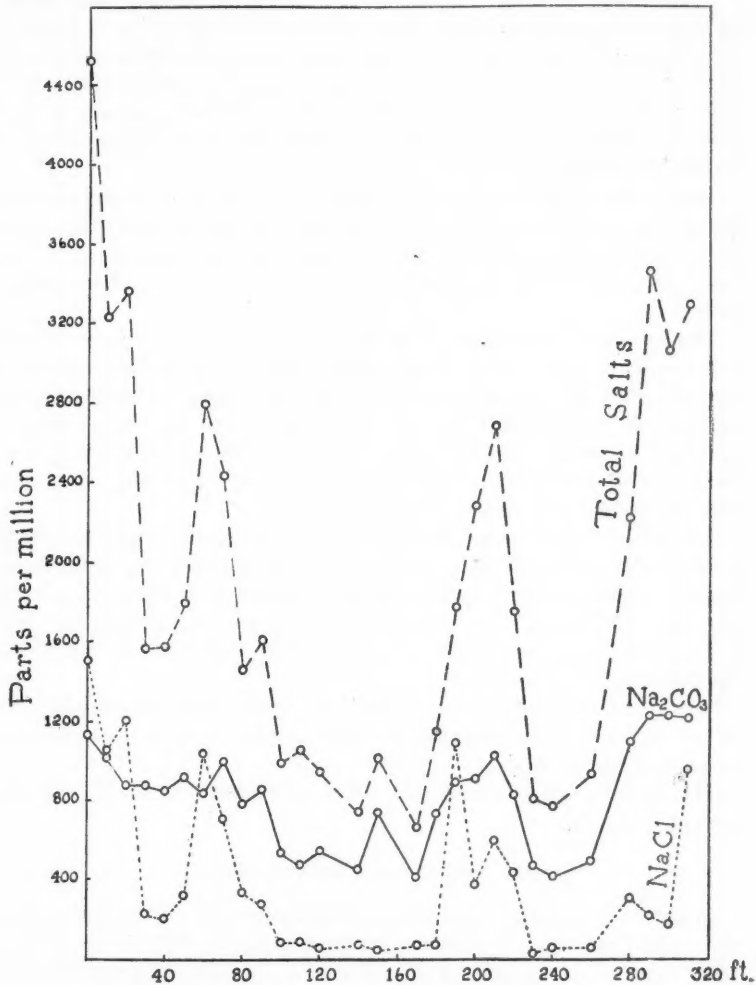


FIG. 1. GRAPHS SHOWING THE LINEAR VARIATION OF AN ALKALI SOIL, FIRST FOOT, PLOT 3  
 $\text{Na}_2\text{CO}_3$  calculated from methyl orange titrations

On that portion of plot 3 from which samples 1 to 9 inclusive were taken, the barley crop was a complete failure. Among these samples, 4, 5 and 6, representing the first foot, contained quantities of chloride, sulfate and nitrate,



each of which is certainly below the limits of toxicity, but here, as is the case with the larger portion of this area, toxic concentrations of sodium carbonate occur.

A sparse stand of barley, varying from 10 to 30 inches in height, was obtained on those portions of plot 3 from which samples 9 to 16 and 22 to 24 inclusive, were taken. It is interesting to note that these samples contained considerably lower concentrations of salts than the other samples from this plot. It is quite probable that the concentration of sodium carbonate present in these spots was sufficiently high to be injurious, although not so high as entirely to prevent the growth of barley.

The portions of plot 8 from which samples 1 to 8 and 26 to 30 inclusive were drawn, were entirely destitute of vegetation. It will be noted that, while all of these samples contained relatively high concentrations of sodium carbonate, several of them contained rather low concentrations of the neutral salts.

The portion of plot 8 from which samples 9 to 25 inclusive were drawn is not an alkali soil. None of the samples from it contained an excess of any salt, although this small area is entirely surrounded by highly saline or alkaline soil. Although this spot is practically free from alkali salts, it produced a very low yield of barley. It will be shown subsequently that the inferiority of the barley here was due to the severity of the competition with several different species of weeds.

The samples representing the second foot were usually found to contain lower concentrations of salts than those of the first foot. In a few cases, however, greater amounts of chloride and sulphate were found than in the first foot. With only a few exceptions, the samples representing the third and fourth feet contained still lower concentrations of salts than the corresponding samples of the second foot.

The almost complete absence of nitrate in certain places was probably due, in part at least, to the fact that the samples were taken in close proximity to growing barley or weeds.

The data as a whole indicate that sodium carbonate is by far the most important salt in this soil.

#### *Samples from specially chosen locations*

In order to study the variability of other portions of this quarter section, three additional series of samples were taken in April, 1921. Two of these, series A and B, were drawn from a line of holes extending perpendicularly across the margins of alkali spots, a part of each series being taken from barren soil and a part from fairly productive soil. The distance between the places of sampling was either 2 or 3 feet. The analysis of series A and B is recorded in tables 5, 6, 7 and 8.

The composition of the samples composing series A varied quite widely. Among those representing the first foot, sample 3 contained more than three

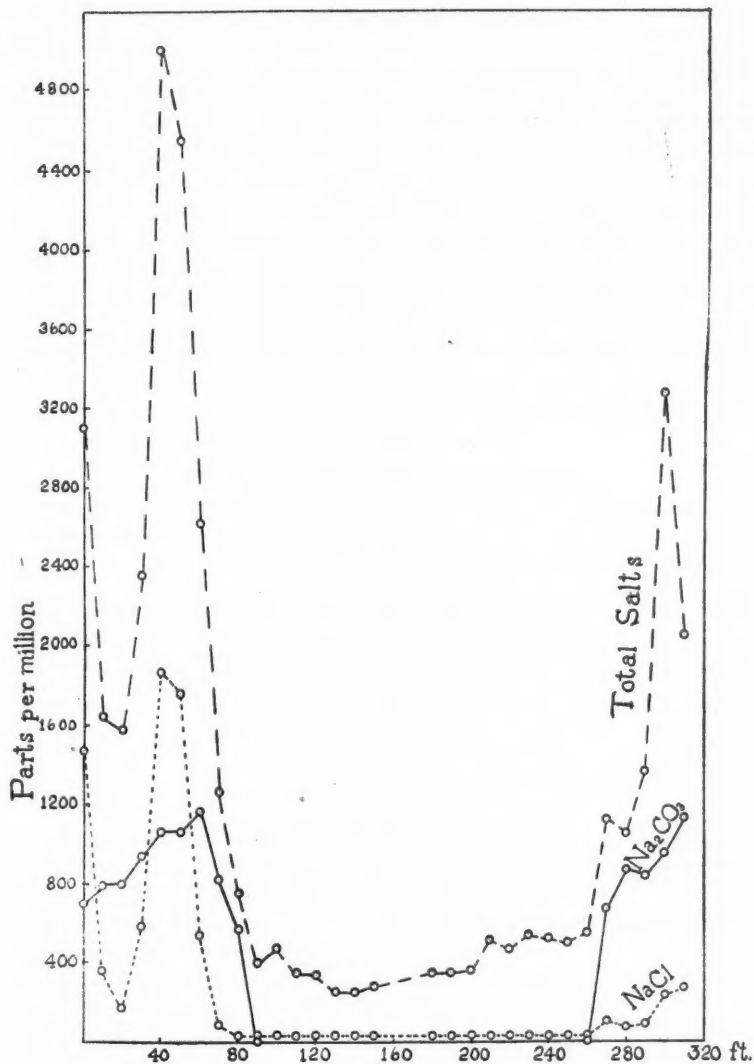


FIG. 2. GRAPHS SHOWING THE LINEAR VARIATION OF AN ALKALI SOIL, FIRST FOOT, PLOT 8

Na<sub>2</sub>CO<sub>3</sub> calculated from methyl orange titrations unless extract failed to give a reaction with phenolphthalein and also contained a substantial amount of calcium.

TABLE 5  
Composition of soil samples, series A, first foot

SAMPLE NUMBER AND DISTANCES	1	2 3 FT. FROM 1	3 3 FT. FROM 2	4 2 FT. FROM 3	5 2 FT. FROM 4	6 2 FT. FROM 5	7 2 FT. FROM 6	8 2 FT. FROM 7	9 2 FT. FROM 8
Growth of barley	None	None	None	None	Slight stand, 12 in. high	Thin stand, 18 in. high	Fair stand, 30 in. high	Good stand, 36 in. high	Good stand, 36 in. high
<i>Parts per million</i>									
CO <sub>2</sub> .....	420	300	255	270	270	210	0	0	0
HCO <sub>3</sub> .....	320	366	381	412	259	259	335	335	320
Cl.....	355	514	798	222	168	133	496	115	62
SO <sub>4</sub> .....	202	303	443	61	62	13	170	110	11
NO <sub>3</sub> .....	89	62	7	4	0	0	9	0	0
Total salts...	2400	2700	3240	1680	1355	1035	1450	1125	735
pH value....	9.6	9.6	9.5	9.6	9.6	9.6	7.3	7.7	8.2

TABLE 6  
Composition of soil samples, series A, second foot

SAMPLE NUMBER	1	2	3	4	5	6	7	8	9
<i>Parts per million</i>									
CO <sub>2</sub> .....	150	135	150	75	180	180	0	15	15
HCO <sub>3</sub> .....	183	229	244	274	229	214	442	305	290
Cl.....	177	186	390	106	177	142	213	248	97
SO <sub>4</sub> .....	37	52	179	33	43	16	67	90	13
NO <sub>3</sub> .....	19	18	5	4	0	0	9	0	0
Total salts.....	1000	1085	1665	720	1155	950	910	1150	710
pH value.....	9.4	9.3	9.4	9.2	9.6	9.6	8.0	8.6	8.8

TABLE 7  
Composition of soil samples, series B, first foot

SAMPLE NUMBER AND DISTANCES	1	2 3 FT. FROM 1	3 3 FT. FROM 2	4 2 FT. FROM 3	5 2 FT. FROM 4	6 2 FT. FROM 5	7 2 FT. FROM 6	8 3 FT. FROM 7
Growth of barley	None	None	None	None	Slight stand, 12 in. high	Thin stand, 24 in. high	Good stand, 30 in. high	Good stand, 36 in. high
<i>Parts per million</i>								
CO <sub>2</sub> .....	285	270	300	195	90	90	45	30
HCO <sub>3</sub> .....	274	366	290	335	473	366	442	412
Cl.....	44	62	35	71	97	160	168	133
SO <sub>4</sub> .....	67	64	73	62	31	69	43	134
NO <sub>3</sub> .....	0	5	7	5	9	4	0	5
Total salts.....	1100	1200	1075	970	1180	1100	925	1000
pH value.....	9.6	9.6	9.6	9.6	9.2	9.2	9.1	9.0

times as much chloride as sample 4 taken two feet distant, and number 7, contained approximately 4 times as much chloride as number 8. It will be noted that considerable amounts of sodium carbonate were found in each sample of the barren soil, while none was found in the first foot of the soil where reasonably good growth of barley occurred. However, substantial amounts of sodium bicarbonate were found in these latter samples, and both sodium carbonate and sodium bicarbonate occurred in all but one of the corresponding samples of the second foot. It is quite possible that the growing barley gave off  $\text{CO}_2$  in amounts sufficient to convert the normal carbonate of the first foot into the bicarbonate.

Each sample of series B contained very low concentrations of the neutral salts, but again, the barren portion contained rather high concentrations of sodium carbonate. It will be noted also that small amounts of sodium carbonate were found where a fair crop of barley was secured, but in this case the second foot, with the single exception of sample number 8, contained considerably less normal carbonate than the first foot.

TABLE 8  
*Composition of soil samples, series B, second foot*

SAMPLE NUMBER	1	2	3	4	5	6	7	8
<i>Parts per million</i>								
$\text{CO}_3$ .....	60	105	120	60	15	0	15	45
$\text{HCO}_3$ .....	274	198	244	274	305	274	274	290
Cl.....	115	97	89	106	160	115	62	80
$\text{SO}_4$ .....	41	41	47	41	82	31	17	Trace
$\text{NO}_3$ .....	0	0	0	3	5	0	5	0
Total salts.....	800	800	820	760	920	650	390	575
pH value.....	9.2	9.2	9.5	8.8	8.8	8.0	8.8	9.2

The samples composing series C were taken at a uniform distance of two feet apart. The area sampled was entirely devoid of vegetation. Barley seeds had failed to germinate on this spot for several years previously. The analysis of the first, second, third and fourth feet, respectively, are submitted in tables 9, 10, 11 and 12.

It will be noted that the chloride, sulphate, nitrate and total salts varied greatly. Among the samples of the first foot, number 8, for example, contained more than five times as much chloride, sulphate and nitrate as sample 9 taken just two feet away. Other samples (4 and 6) taken 4 feet apart, varied more than four-fold while in one instance samples taken 6 feet apart (6 and 9) showed more than a ten-fold difference in their neutral salts. On the other hand, the content of alkali carbonate was comparatively constant throughout this series.

Considerable variation was also noted among the samples from the second, third and fourth feet. Two of the samples (9 and 10) contained greater

amounts of chloride and sulphate in the second than in the first foot, while the reverse is true of the other samples.

TABLE 9  
*Composition of soil samples, series C, first foot\**

SAMPLE NUMBER	1	2	3	4	5	6	7	8	9	10
<i>Parts per million</i>										
CO <sub>2</sub> .....	465	390	360	420	360	525	450	285	420	450
HCO <sub>3</sub> .....	305	320	457	305	457	335	214	640	214	335
Cl.....	2080	1968	1914	656	1489	2659	1452	1179	177	674
SO <sub>4</sub> .....	1844	1148	1030	433	1098	2012	735	575	55	506
NO <sub>3</sub> .....	400	250	249	89	312	481	267	223	43	116
Total salts.....	7740	7070	6555	3085	5955	10250	5130	4900	2405	3770
pH value.....	9.6	9.6	9.6	9.6	9.7	9.8	9.8	9.3	9.6	9.8

\* Samples were taken 2 feet apart.

TABLE 10  
*Composition of soil samples, series C, second foot*

SAMPLE NUMBER	1	2	3	4	5	6	7	8	9	10
<i>Parts per million</i>										
CO <sub>2</sub> .....	300	360	360	360	375	300	270	240	330	300
HCO <sub>3</sub> .....	274	244	259	198	244	305	366	290	214	290
Cl.....	833	638	381	567	780	1072	372	523	1028	1117
SO <sub>4</sub> .....	608	218	95	207	340	410	76	128	709	655
NO <sub>3</sub> .....	142	85	46	62	134	151	53	89	169	116
Total salts.....	3110	2570	1820	2375	2515	3555	1850	2325	4170	4200
pH value.....	9.6	9.6	9.6	9.6	9.7	9.8	9.7	9.3	9.6	9.6

TABLE 11  
*Composition of soil samples, series C, third foot*

SAMPLE NUMBER	1	2	3	4	5	6	7	8	9	10
<i>Parts per million</i>										
CO <sub>2</sub> .....	315	330	300	300	270	240	240	240	210	315
HCO <sub>3</sub> .....	335	274	214	366	305	305	351	320	229	259
Cl.....	355	266	381	230	195	355	186	275	239	301
SO <sub>4</sub> .....	107	100	84	31	41	124	11	46	41	42
NO <sub>3</sub> .....	53	29	37	23	20	50	15	32	29	22
Total salts.....	1850	1650	1675	1365	1280	1695	1220	1075	1435	1650
pH value.....	9.6	9.6	9.3	9.7	9.2	9.6	9.4	9.5	9.2	9.6

TABLE 12  
Composition of soil samples, series C, fourth foot

SAMPLE NUMBER	1	2	3	4	5	6	7	8	9	10
<i>Parts per million</i>										
CO <sub>3</sub> .....	180	150	150	165	60	60	90	75	90	330
HCO <sub>3</sub> .....	320	335	305	274	305	351	214	351	259	168
Cl.....	257	319	142	97	142	346	177	133	115	230
SO <sub>4</sub> .....	83	98	58	21	47	181	43	34	31	62
NO <sub>3</sub> .....	24	20	12	9	12	26	18	15	11	18
Total salts.....	1320	1400	920	930	675	1280	835	830	900	1485
pH value.....	9.4	9.5	9.0	8.9	8.7	8.9	8.9	9.0	8.9	9.7

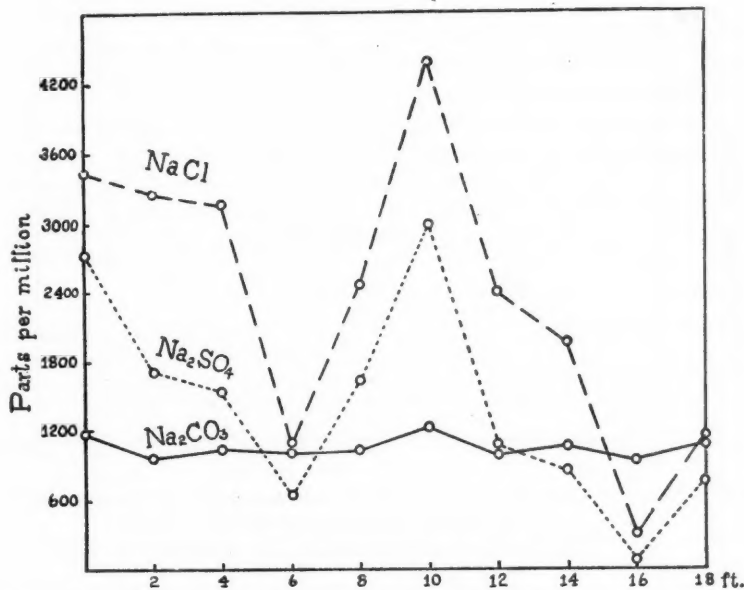


FIG. 3. GRAPHS SHOWING THE LINEAR VARIATION OF AN ALKALI SOIL AT DISTANCES OF TWO FEET APART, FIRST FOOT, SERIES C  
Na<sub>2</sub>CO<sub>3</sub> calculated from methyl orange titrations

#### DISCUSSION

The preceding data show that the amount of some one or more of the soluble salts in soil samples taken from a very small area varied enormously. The distribution of chloride and sulphate was especially variable. Samples taken only 2 feet apart showed a difference of more than 600 per cent in chloride and more than 1000 per cent in sulphate content. As is illustrated by the graphs,

the concentration of the several neutral salts was much more variable than that of the alkali carbonates, although the distribution of the latter was far from being uniform.

It is evident from these data that the analysis of a single soil sample drawn from one place within the area studied, has very little value. It was found, for example, that one or more samples from each of several of the experimental plots contained practically no alkali salts; other samples contained high concentrations of one or more salts; and still others had a composition intermediate between these extremes. If similar variation characterizes the distribution of salts in alkali soils generally, it may be safely concluded that the analysis of

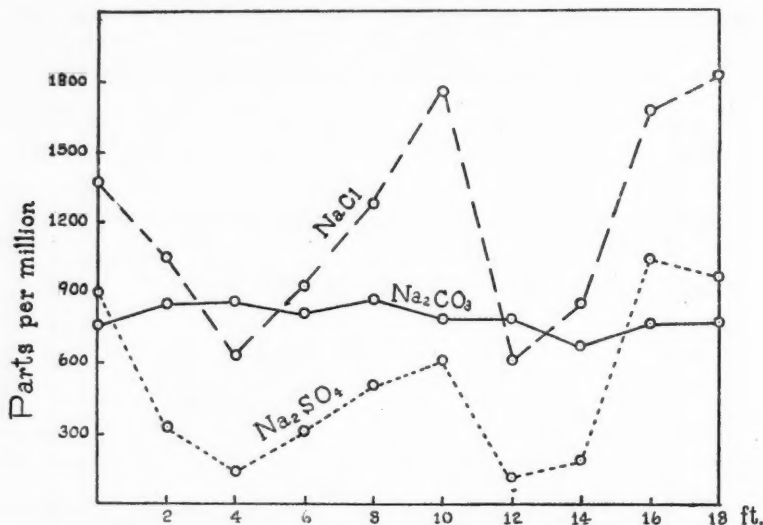


FIG. 4. GRAPHS SHOWING THE LINEAR VARIATION OF AN ALKALI SOIL AT DISTANCES OF TWO FEET APART, SECOND FOOT, SERIES C

Na<sub>2</sub>CO<sub>3</sub> calculated from methyl orange titrations

samples such as are commonly submitted by practical farmers is a waste of time. In fact, the conclusions that are likely to be drawn from the analysis of such samples may be so erroneous as to lead to the recommendation of practices the very opposite of those that should be employed.

The character of the vegetation probably affords one of the safest guides in the sampling of an alkali soil. Wherever noticeable differences occur in the vigor of a given species or in the distribution of different species, there is likely to be some difference in the salt content of the soil. Poor growth of a crop, however, does not necessarily denote alkali soil, for any or all of the factors which limit plant growth in humid regions, many of which are very imperfectly understood, may be present in the soils of alkali regions.



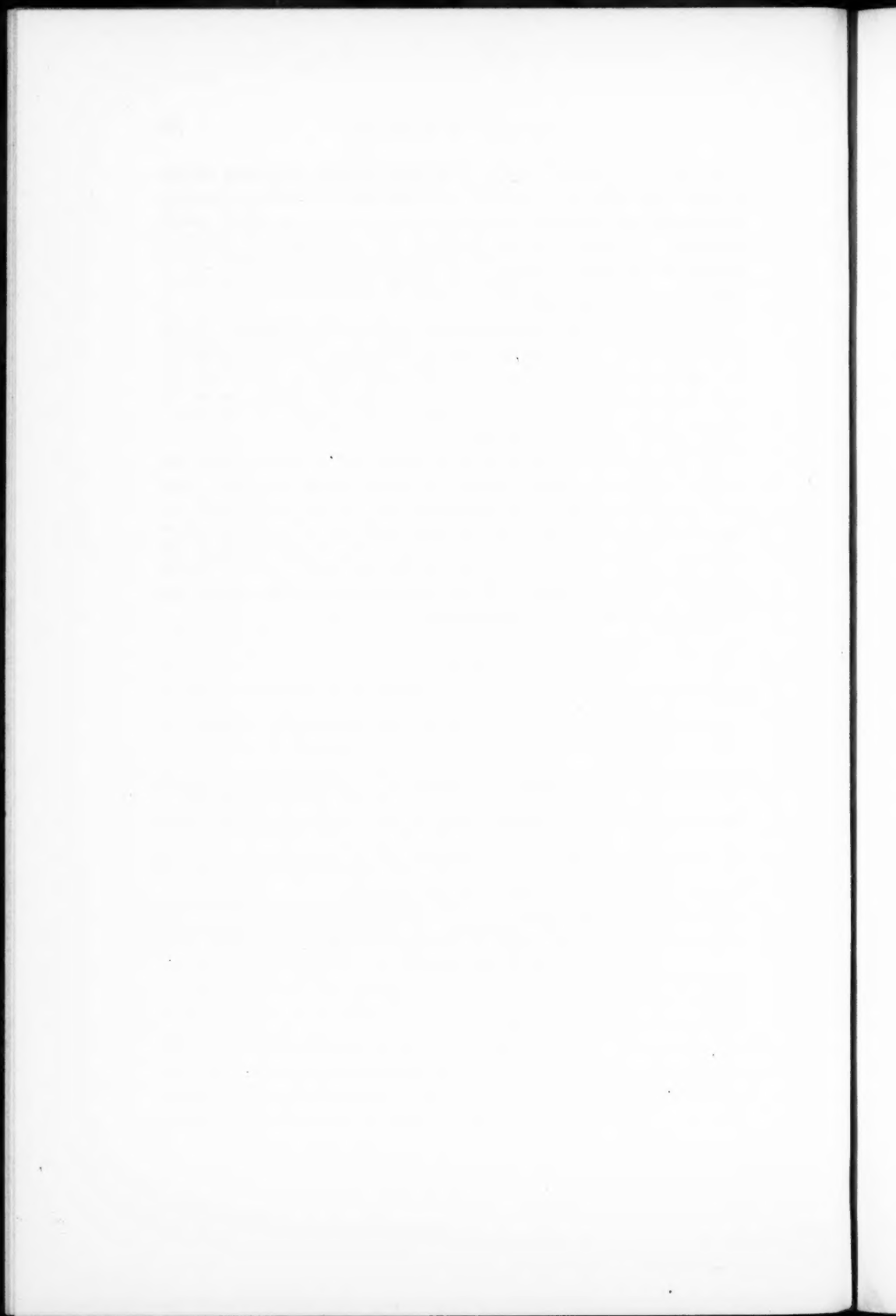
It seems quite doubtful whether a composite sample of an alkali soil can be relied upon unless it be composed of a large number of individual samples each of which was taken from an area in which the variation lies within reasonable limits. At present it is not possible to say what number of individual samples will be required to determine the mean composition of a given area of alkali soil. If the area be of considerable size the number of samples is reasonably certain to be very large.

In a subsequent paper the reclamation of this soil will be discussed. It is of interest to point out at this time that the application of a given treatment has already proved highly successful with certain parts of these plots and quite unsuccessful on other parts. In undertaking plot experiments on this or other similar soil, it is scarcely possible to over-emphasize the importance of the extreme variability of the soil.

The above results suggest some of the reasons why it is often found difficult to determine the alkali tolerance of plants. In the first place, alkali soils usually contain more than one kind of salt. In the second place, it is rare that the concentration of one salt varies while that of the others remains constant. Thirdly, the soil on one side of a plant may be highly charged with salts and on the other side comparatively free from salts. In view of these facts it is doubtful whether an accurate determination of alkali tolerance can be made by means of field cultures alone.

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# THE SOIL SOLUTION, EXTRACTED BY LIPMAN'S DIRECT-PRESSURE METHOD, COMPARED WITH 1:5 WATER EXTRACTS

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## INTRODUCTION

The physical, chemical and biological complexity of arable soils is everywhere recognized. Soils may be considered as being made up of three distinct classes of physical components or phases; the solid, the liquid and the gaseous. Until recent years the solid phase has received the lion's share of attention, but we are beginning to realize the importance of more definite knowledge concerning the gaseous and especially the liquid portion of soils. This is necessary if we are to understand more perfectly soil interrelationships and physiological plant processes. The analysis of soil gases has from early times been a subject of interest and somewhat extended study, especially the oxygen: carbon-dioxide ratio.<sup>2</sup> The liquid phase, however, as it exists in the interstices and as it intimately surrounds the soil particles at approximately optimum moisture content, although receiving much opinionated theoretical discussion, has to its credit a surprising lack of experimental data. This, of course, is due to the fact that numerous difficulties are at once encountered when one attempts to separate the natural soil solution from its harboring solid phase.<sup>3</sup> That a furtherance of our knowledge of this, the universal plant nutrient solution, is indispensable to the advancement of our science, is now admitted by most students of soils. At one time it was contended that all normal, tillable soils contain solutions of approximately equal concentrations, and that work on solutions from different soils was but a repetition of effort. This erroneous theory has fortunately been refuted and the value of

<sup>1</sup> The work herein reported was performed in the laboratories of the University of California.

It is a pleasure to the writer sincerely to thank Dr. C. B. Lipman, Dr. W. P. Kelley and Prof. D. R. Hoagland for their many helpful suggestions and timely criticisms.

<sup>2</sup> The more recent and exacting work of Russell and Appleyard in England, Lyon and Bizzell in America, and Harrison, et al., in India has greatly extended our knowledge along this line.

<sup>3</sup> Quincke's figures show that solid particles the size of "clay" are able to hold thin water films to their surfaces with a force equivalent to approximately 300,000 pounds to the square inch, while Lord Rayleigh, from certain experimental data, calculated that thin films of liquids (water among them) were held to certain surfaces with a force of 25,000 atmospheres per square inch.

such studies is now widely recognized. Not only is it desirable to ascertain the ratios, and absolute concentrations of the so-called mineral nutrient elements dissolved in soils of different productive capacities, but also is a knowledge of the concentrations of certain inorganic toxic substances, such as aluminum, manganese, ferrous iron, hydrogen ions, and the so-called "alkali salts," in the soil solution<sup>4</sup> of decided importance. Exact quantitative knowledge regarding the natural liquid phase of soils may further enable us to evaluate more accurately the data obtained by means of water extracts. Definite knowledge concerning the natural soil solution is necessary to an understanding of soil-fertility problems. And finally, those minute and indispensable allies to continuous productivity, the soil microorganisms, live, function in and derive their food supply from this same imperfectly known soil solution.

The present paper presents a quantitative chemical study of the liquid phase of soils as extracted by a direct pressure method. The idea of using heavy pressures, as secured on large testing machines, for this purpose was proposed by Lipman (10) in 1918 after a few preliminary experiments had shown its feasibility. The procedure was at the time quite severely and somewhat caustically criticized by Northup (15). That this criticism was founded largely upon opinion, and can hardly be said to have been substantiated by fact, will be shown by subsequent data.

#### PREVIOUS WORK

It is not the purpose of the writer to review all of the past attempts at securing the soil solution as it exists naturally in soils. This has been quite fully done by Morgan (14) on two separate occasions. He groups such procedures under the general headings of drainage waters, soil extracts, artificial roots, centrifuge and displacement methods. No mention was made by him of direct-pressure or "squeezing" methods, although a few such attempts have been recorded.

Probably De Saussure (19) was among the first to secure a portion of the soil solution for analytical purposes. Direct pressure applied to the moist soil was used by him. He filled large vessels with soils containing considerable quantities of humus. These were then saturated with pure water and allowed to drain for a period of five days. The soils were then subjected to powerful pressures and the water thus extracted was analyzed quantitatively for carbon dioxide and tested qualitatively for other substances.

More recently van Zyl (23), experimenting largely with clay soils, employed direct pressure. He found no difficulty in securing considerable quantities of soil solution by this means. Analyses of such solutions from different soils showed decided differences in the amounts of

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<sup>4</sup> The reader should not confuse the terms "soil solution" and "soil extract." The former is the soil water as it exists naturally in normal field soils, while the latter is a solution secured by extracting a soil with various solvents, usually used in excess of soil weight, and under decidedly artificial conditions. The several solvents employed in such extractions may yield solutions far removed in quantitative composition from the true soil solution.

plant food constituents present. He stated that this was due to previous fertilization and to climatic factors.

Studies later conducted at the University of Göttingen by Ehrenberg and van Zyl (6) on soil solutions are also of interest. Loam and clay soils were subjected to high pressures, using heavy hydraulic presses of great capacity. Comparisons of solutions thus obtained from soils differently fertilized are reported. Unfortunately the pressures used were not stated.

Ramann, März and Bauer (18), after having shown drainage waters to reflect but poorly the composition of true soil solutions, also adopted the method of forcing the capillary water out of soils as taken from the field, with a hydraulic press. They employed a pressure of 300 kgm. per sq. cm. (4300 lbs. per sq. in.). The expelled liquids were analyzed for calcium, magnesium, potassium, phosphoric acid, and sulfates. The soil samples were taken once each month, beginning in May and ending with October. Both surface soils and subsoils were used. The monthly variations of the different ions under growing crops were discussed, together with the effects of climatic factors on the fluctuations noted. The solutions obtained from the subsoils were all of fairly constant composition and of low concentration.

A rather ingenious method of obtaining the soil solution was recently proposed by Taylor (22). He buried pads of absorbent filter paper in moist soils for definite lengths of time and then extracted the absorbed solutions from the pads by subjecting them to high pressures. The solutions thus procured were subsequently analyzed as were the soils themselves (acid extraction). By a comparison of such analyses it was concluded that "the composition of the soil water is not that which would be inferred from the chemical analysis of the corresponding soil."

An interesting paper, reviving the old alcohol-displacement method proposed nearly fifteen years ago by Ischerekov (9), has recently appeared by Parker (16) in which yields of 36 to 75 per cent of the total soil solution were obtained. A few preliminary experiments by the writer showed displacements approaching 60 per cent for fine sandy and silt loams, but for the heavier soils, several days were often required in securing a small fraction of the soil solutions present at optimum moisture contents. The method, however, has promise and should receive the careful consideration of soil chemists.

Before taking up a discussion of the direct pressure method for extracting the soil solution, I desire very briefly to record certain experiences with the oil-pressure procedure as suggested by Morgan (14), which were secured at the expense of the Agricultural Experiment Station of the Hawaiian Sugar Planters' Association in Honolulu in 1917 and 1918. Three widely different types of Hawaiian soils were used: clay loams, sandy loams and a highly organic rice soil. Various mechanical devices and different methods of packing the soils were tried. Two grades of paraffin oil (light and medium heavy) were used, and pressures up to 1000 lbs. per square inch were employed. The inside diameter of the cylinder used was 10 inches and its height was 18 inches.

It was found first of all that the oil did not penetrate the soils, forcing the moisture out ahead of it, as was claimed. One inch of penetration was the maximum ever noticed, even in the sandy soils and under pressures up to 1000 pounds per square inch, all due precautions being taken. This was the case irrespective of grade of oil used. The oil under pressure acted as a solid ram or piston. The clay and organic rice soils were very springy, contracting and expanding like a sponge as the pressure was turned on and off, but practically no penetration of the oil into the soil mass was noted. The moisture which was expressed came almost entirely from the lower layers of the soils, as the following figures taken at random from many such data will show:

After pressing 6 hours at approximately 900 pounds,

	per cent
Original (soil No. 1) .....	47.0
Surface 4 inches (next to oil) .....	47.0
Second 4 inches .....	46.1
Third 4 inches .....	45.0
Last 3 inches (next to screens) .....	42.0

(Samples taken from cylinder with auger)

It was also found that but a very small fraction of the total moisture (when the soils are at optimum) can be secured by hydraulic pressures within reason; less than 20 per cent for the sandy soils, less than 2 per cent for the clay loams and less than 10 per cent for the peaty rice soil. In fact, only a few cubic centimeters of solution were secured from 30 to 40 pounds of several of the heavier clay soils pressed at 500 to 800 pounds pressure for several hours.

Finally, as stated by Lipman (10), the method is extremely "time-consuming and untidy." This criticism might well be waived if desirable results had been secured but this can hardly be said to have been the case. It should be borne in mind, however, that the writer here employed Hawaiian soils which differed greatly (both physically and chemically) from the arable soils commonly found on the mainland.

#### THE DIRECT PRESSURE METHOD

The objects of the experiments about to be described were: (1) To separate from the solid soil mass the true soil solution as it exists in soils when they are under approximately optimum moisture conditions for the growth of crop plants; (2) To ascertain the actual concentrations within these solutions of ions essential as food materials for plants; (3) To compare quantitatively these results with data from the same soils obtained by the water-extraction method.

#### *Apparatus employed*

As the name of the method suggests, heavy pressures were applied directly to moist soils held in properly constructed retaining vessels or presses which were provided with suitable exits for the escape of the expelled solutions. The design and construction of the retainers capable of withstanding pressures up to 100,000 pounds to the square inch, which would allow moisture to escape but at the same time hold back even the smallest particles of soils, was a task which consumed by far the larger portion of the total time spent by the writer upon this work, and he wishes here to express to Professor C. T. Wiskocil, in charge of the Testing Laboratories of the Department of Civil Engineering of the University of California, his most sincere thanks for the many helpful suggestions rendered and for the actual design of the last and most efficient press built for this work.

Three different presses were constructed in the machine shops of the Testing Laboratories during the course of the experiments. Press no. 1 was simply an 8-inch cylindrical steel block carrying a 2-inch hole through its center which was carefully finished to receive two movable, hardened and ground steel pistons. The interior was slightly recessed. A finely perforated brass sleeve of the same inner diameter as the pistons was placed in the recess, and thoroughly washed white sand packed between it and the inner wall of the retaining steel block. Through the block an opening for the expressed solution was provided. The soil was packed into the brass sleeve, the pistons inserted, one from the bottom and the other from the top, and the whole placed on the table of a heavy testing machine which supplied the pressure. As will be seen, the washed sand here acted as a filter or soil retainer. This type of press was most efficient in the separation of solutions from heavy clay and clay-loam soils although it was extremely time-consuming in operation.

The second press constructed, Press no. 2 (see plate 1), was the one used for obtaining a majority of the solutions later to be discussed. This one consisted of a heavy steel retaining

block bored out on a slight taper to receive a sectional steel sleeve through which a 2-inch hole was carefully bored and ground to receive the hardened and ground pistons. Many rows of very small holes (one-ten-thousandth of an inch in diameter) were drilled from channels cut lengthwise along the backs of the four pieces of the sectional sleeve into the inner 2-inch finished hole. Through these fine holes the expressed soil solution passed. The taper and collapsible sleeve were made to facilitate the ejection of the hard briquettes of soil after pressing. This press could be efficiently used only with sandy soils, as the finer silts and clay soils were readily squeezed through the small holes. However, with all kinds of sandy soils, even with very fine sandy loams, the apparatus was a decided success, and rapid of operation.

Press no. 3 was without doubt the best one constructed, but it became necessary for the writer to leave California after having worked with it only a short time. It became evident while working with Press no. 2 that the small holes, which were supposed to allow only the solution to pass through, were too large to hold back the smallest soil particles. It was impossible, however, to drill smaller holes, hence some other device was necessary. The making of fine slits, rather than holes, suggested itself. The third press was constructed on this principle, and is shown in plate 2. The moist soil was packed into the center hole, as in the other presses described, and the pistons inserted and forced together against the soil by one of the testing machines. With all presses, considerable trouble was at first experienced because the finer textured soils crept back past the pistons in thin ribbons when the pressure was first applied. However a thin layer of washed sand next to the piston ends permanently overcame this difficulty.

The machines which supplied the pressure were of standard heavy types as found in laboratories where building materials are tested. Three machines were used at different times, one capable of giving 50,000 pounds total pressure per square inch, one of 100,000 pounds capacity (see plate 2), and one of 500,000 pounds capacity. The first two were motor-driven; the last, of hydraulic ram type. The smallest machine was usually employed since no moisture was expressed from the fine sandy loam soils at pressures above 16,000 pounds per square inch.

#### *The soils employed*

Much work has been reported during the past few years by Burd (2), Hoagland (7) and Stewart (21) of the California Agricultural Experiment Station on the effects of plant growth and season upon the concentrations of the soil solution as periodically manifested by water extracts of cropped and fallowed soils. Since an important feature of this present investigation was to compare water extracts with actual soil solutions, it was thought advisable to use the same soils for this work as had been employed previously by the above-named investigators. Through their courtesy sufficient quantities of certain of these soils were placed at the writer's disposal. They had been collected in 1914 and 1915, and since that time had been stored in water-tight bins in an air-dried condition. The numbers originally given to these soils have been retained throughout the present work. A brief description of the samples follows. All are California soils and have been mapped and named by the Bureau of Soils, United States Department of Agriculture.



*Soil no. 7.* Hanford fine sandy loam. From Arlington, southern California. Oats on land when sampled. Past treatment: originally grain; about 1890 put into alfalfa for 13 years; potatoes 2 years; alfalfa 4 years; oats 5 years. Yield of oats: 4 tons of hay per acre.

*Soil no. 8.* Fresno fine sandy loam. From Fresno, San Joaquin Valley. Seedless grapes on land when sampled. Past treatment: originally grain; 14 years in Sultanina grapes. Production: about 2 tons of raisins per acre for the last 6 years.

*Soil no. 9.* Kimbal fine sandy loam. From Redlands. Navel oranges on land when sampled; 25 years in oranges; formerly desert land. Heavily fertilized.

*Soil no. 10.* Tejunga fine sandy loam. From San Fernando Valley, southern California. Peaches on land when sampled; originally 15 years in prunes; last 10 years in peaches. Some stable manure used.

*Soil no. 11.* Madera fine sandy loam. From Kearney Park, San Joaquin Valley. Navel oranges on land when sampled; in oranges for past 15 years; formerly in grain. Well fertilized.

*Soil no. 12.* Yolo sandy loam. From the University Farm at Davis, Sacramento Valley. This soil has been cropped to grain (wheat or barley) since about 1860.

*Soil no. 14.* Standish fine sandy loam. From the Honey Lake region, northern California. Virgin, desert soil; small shrubs and weeds, natural growth.

*Soil no. 3.* Imperial Valley silt. This sample was not secured from Professor Burd, but was collected by the writer in 1915 from near Holtville in the center of the Imperial Valley, southern California. It is a virgin, desert soil supporting a sparse growth of grease-wood (*Sarcobatus vermiculatus*) and creosote bushes (*Covillea Mexicana*). Annual rainfall, 2 to 4 inches.

Table 1 (21, p. 321) gives the moisture equivalents (method of Briggs and Shantz), hygroscopic coefficients (method of Hilgard), and the mechanical analyses (method of Bureau of Soils) of the soils used. From these data a fair idea of the physical properties of the several soils may be formed.

TABLE 1  
*Physical characteristics of soils employed*

SOIL NUMBER	MOISTURE EQUIVA- LENTS	HYGRO- SCOPIC COEF- FICIENTS	MECHANICAL ANALYSES				
			Coarse and medium sand	Fine sand	Very fine sand	Silt	Clay
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
7	13.31	2.89	5.69	15.60	53.67	16.01	9.77
8	8.06	1.17	5.14	21.22	50.63	17.57	5.56
9	9.87	1.53	16.30	21.73	43.67	10.87	8.19
10	18.38	2.94	4.51	16.62	38.76	26.25	13.37
11	16.28	3.16	5.59	20.95	39.34	19.08	14.62
12	9.72	1.77	9.37	23.27	46.24	9.61	9.44
14	17.99	4.74	7.14	24.54	38.94	15.55	13.87

#### *Preliminary experiments*

In order to establish certain important facts as well as to answer certain criticisms (15) of the pressure method, a number of preliminary experiments were first performed. It was deemed necessary to ascertain the effect of the different pressures upon total soil solubility, upon the specific gravity of the soil solutions extracted, upon their specific conductivities and upon the solubilities of the more important elements. Furthermore, it was thought

desirable to know whether such pressures would effect a measurable fining or abrasion of the soil particles, thereby exposing fresh surfaces to the solvent action of the soil moisture during extraction. We realized that bacteria are killed at high pressures, hence no work of a bacteriological nature was attempted on any of the solutions obtained.

An increase in pressure has been supposed to enhance the solvent action of water on minerals and soils, but so far as the writer has been able to find, little direct proof of this fact is extant. That this supposition, in some cases at least, is erroneous has been shown by Spezia, by Tammann and also by Van Stackelberg (4, p. 31). While there is some geological evidence to show that the solvent action of water at great depths in the earth's crust is slightly greater than at the surface, Cameron and Bell (4) state that probably here the increases are largely due to higher temperatures and to the increased concentration of gases in solution, notably carbon dioxide. Some work has been done on the effect of direct pressures on the solubilities of salts dissolved in pure water, but here again the data is meager and often conflicting, as in the well-known case of ammonium chloride. It would seem probable that slight temperature fluctuations while working at high pressures might possibly account for very small differences occasionally noted, for while temperature change makes a vast difference in degree of solubility, exceedingly high pressures even upon concentrated solutions are required to effect the smallest measurable differences. In the light of such data as was available and in the light of information obtained by discussing the subject with chemists, it hardly seemed probable that great differences would be found in the concentrations of so dilute a solution as the natural soil water as a result of the pressures here employed.

In an endeavor to test this matter experimentally the expressed solutions from a number of soils were obtained in fractions depending upon the pressures used and determinations were made of the total soluble solids, soluble organic matter and dissolved inorganic matter on aliquots of these several fractions. The soils were kept under approximately optimum moisture conditions for two or three days immediately before pressing. Those here used were all sandy loams of varying degrees of fineness. The three fractions were so regulated as to give approximately equal volumes of solution. The results appear in table 2.

As will be seen by studying these data, the quantity of materials dissolved in the different fractions of the soil water extracted from a given soil under different pressures varied but slightly in amount. This holds for the organic as well as for the inorganic solids. It is thus highly probable that the heavier pressures used had but slight effect, if any, on the amounts of materials which were dissolved in the solutions of the three soils prior to pressing. *We cannot, of course, be sure that the higher pressures, or the lower ones for that matter, were actually applied to the liquid phase itself, as this was always free to escape.* It would seem somewhat more probable that most of the force was utilized in overcoming the friction of the solid phase caused by its compression

into a slightly smaller space. From the above data it would also appear that the solutions remaining in these soils after applying the pressures were probably of similar concentration to those removed, and that still greater amounts of solution might have been obtained had the solid particles of the soil been of a more yielding or compressible nature.

The specific gravities of the three fractions of soil solution removed from soil 12 were determined by the picnometer method. The results were as follows:

	<i>specific gravity</i>
First fraction (0-1600 lbs.)	1.0010
Second fraction (1600-5730 lbs.)	1.0009
Third fraction (5730-15925 lbs.)	1.0010

As the results here secured are very nearly identical, and as determinations subsequently made practically proved the identity of the several fractions, this determination was not made on the fractions of the other soil solutions obtained.

TABLE 2  
*The effect of different pressures on soil solubilities*

SOIL NUMBER	PRESSURE FRACTION	WATER EXTRACTED FROM EACH 400-GM. CHARGE OF MOIST SOIL	TOTAL SOLUBLE SOLIDS	INORGANIC SOLUBLE SOLIDS	ORGANIC SOLUBLE SOLIDS
	<i>lbs. per sq. in.</i>	<i>cc.</i>	<i>p.p.m.*</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
12	0- 1600	12-13	1340	890	450
12	1600- 5730	10-11.5	1310	870	440
12	5730-15925	7- 8	1350	860	490
10	0- 1600	15	2120	1000	1120
10	1600- 5730	14-15	2240	1090	1150
10	5730-15925	12-13	2280	1020	1260
7	0- 1600	14	1610	810	800
7	1600- 5730	15-16	1750	910	840
7	5730-15925	11-12	1760	920	840

\* Parts per million of soil solution.

Specific resistance (the reciprocal of specific conductivity) determinations were made on all of the fractions secured. While this determination does not show the concentration of non-electrolytes and of un-ionized electrolytes, it was thought to be of importance as a sensitive indicator of total ionic concentration, and due to its dilution, the mineral or salt content of the soil water was thought to exist very largely in the ionic state. Table 3 presents these data.

The specific resistances of the several pressure fractions from each of the three soils are within the limits of experimental error, denoting almost identical ionic concentrations in each case.

As a final test on the chemical similarity of the solutions secured at different pressures, calcium and magnesium determinations were made on the several fractions. These two elements were chosen as here best reflecting ionic con-

centrations in general for they were known to be present in largest amounts, would thus be able to be determined with greatest accuracy in the small amounts of solution available, and would finally be capable of best showing small fluctuations in concentration. These data appear in table 4.

These data, taken in conjunction with those previously presented, would seem to prove that, with fine sandy loam soils at least, the application of direct pressures up to approximately 16,000 pounds per square inch has little, if any, effect on the quantitative composition of the expressed solutions, and suggest that the concentration of that part of the soil water which remained

TABLE 3  
*Specific conductivities of soil solutions extracted at different pressures*

SOIL NUMBER	PRESSURE FRACTION	SPECIFIC RESISTANCE
	<i>lbs. per sq. in.</i>	<i>ohms</i>
12	0- 1600	614.4
12	1600- 5730	624.6
12	5730-15925	627.2
10	0- 1600	354.6
10	1600- 5730	364.8
10	5730-15925	369.3
7	0- 1600	448.0
7	1600- 5730	450.6
7	5730-15925	444.8

TABLE 4  
*Calcium and magnesium determinations on soil solutions extracted at different pressures*

SOIL NUMBER	PRESSURE FRACTION	CALCIUM	MAGNESIUM
	<i>lbs. per sq. in.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
12	0- 1600	150	87.5
12	1600- 5730	152	89.0
12	5730-15925	150	88.0
10	0- 1600	147	30.5
10	1600- 5730	165	37.1
10	5730-15925	165	36.0

in the soil after pressing probably carried similar amounts of solutes at the time of extraction.

The last test of the method was made in an endeavor to determine whether or not there was a grinding or fining of the soil when pressures of 16,000 pounds per square inch or less were applied. Such action, if it took place, might have a tendency to alter slightly the chemical composition of the resulting solution by exposing the fresh cleavage surfaces of the mineral particles to the dissolving effect of the liquid phase. McCool and Millar (12), working with the cryoscopic method, have, in fact, recently shown that grinding soils increases their solubility in distilled water, marked changes being observed in less than 24

hours. Suspension or subsidence tests were accordingly made on the moist soils, both before and after pressing, as follows: The equivalent of 10 gm. of water-free soil was triturated in a little distilled water with a rubber-tipped pestle to break up all lumps. These suspensions were then made up to exactly 250 cc. and shaken for 1 hour in a shaking machine when they were immediately poured into tall, glass-stoppered, graduated cylinders of the same bore and height, and allowed to settle for varying lengths of time, depending upon texture. Exactly 50 cc. of the turbid suspensions were then carefully removed from the surface of each cylinder, evaporated to dryness and the solid matter gravimetrically determined. In several cases the coarser particles which settled to the bottom were examined under a microscope in an endeavor to locate freshly chipped or abraded surfaces. The data obtained from the suspension experiments appear in table 5.

As will be seen, the solid matter in the several subsidence fractions which were at the top and obviously carried the smallest particles of the soils, was not

TABLE 5  
*Suspension tests to note the effect of pressure on abrasion of soil particles*

SOIL NUMBER	PERIOD OF SUBSIDENCE	SUSPENDED MATTER BEFORE PRESSING	SUSPENDED MATTER AFTER PRESSING
	<i>hours</i>	<i>p.p.m.*</i>	<i>p.p.m.*</i>
12	4.5	1390	1354
10	2.5	2050	1820
7	1.5	1530	1600
8	8.0	570	740
9	4.5	830	1030
11	5.0	1290	1130

\* Parts per million of suspension.

greatly altered in amount by the pressure treatment. While it is possible that some of the larger particles may have been broken, we are here more especially concerned with the finer portions, for Loughridge (11), and more recently McCool and Millar (12) have shown that practically all of the materials which readily go into solution in soils come from the silt and clay fractions. No definite abrasive action was noted, however, in the microscopical examinations of the larger mineral particles. A complete mechanical analysis might possibly have settled this point better but lack of time prevented such extended preliminary work.

#### *Percentages of soil solution extracted*

It was the practice of the writer to ascertain first the soil's optimum moisture content,<sup>5</sup> bring it up to this percentage with distilled water, and allow it to stand, loosely covered, at room temperature for about a week (moistening when necessary) before the extraction was made. The soil was thoroughly

<sup>5</sup> Fifty per cent of saturation as shown by Hilgard's method.

stirred immediately before pressing and moisture determined. After pressing, another moisture determination was at once made. The difference between these gave the actual percentage of moisture expressed, calculated as percentage of the dry soil.

Table 6 records the percentages of moisture in each soil before and after pressing, the actual percentages of soil water extracted, their wilting coefficients as calculated from the mechanical analyses by the formula proposed by Briggs and Shantz, and the percentages of "unfree water" as calculated for these soils by Hoagland (7) from freezing point determinations.

A perusal of table 6 reveals certain points of interest. The first is that, of the eight fine sandy loam soils moistened to but 50 per cent of their total mois-

TABLE 6  
*Percentages of soil moisture extracted*

SOIL NUMBER	MOISTURE IN SOIL BEFORE PRESSING*	MOISTURE IN SOIL AFTER PRESSING*	MOISTURE EXTRACTED FROM SOIL	WILTING COEFFICIENT (CALCULATED)	"UNFREE WATER" (7, P. 371)
	<i>per cent</i>	<i>per cent</i>	<i>per cent of total</i>	<i>per cent</i>	<i>per cent</i>
3	22.7	9.0	60.3		
7	19.1	6.6	65.4	7.2	6.0
8	18.3	8.7	52.5	4.5†	4.0
9	17.7	9.9	44.8	10.8	6.0
10	23.0	8.4	63.5	10.1	8.0
11	17.8	6.9	61.2	8.9	6.0
12	21.9†	8.0†	63.4	6.6	4.0
14	22.0	10.4	52.7	9.8	7.5

\* Figured on moisture-free basis.

† Moisture data on fractional extractions only were secured.

‡ This wilting coefficient is apparently too low.

ture-holding capacities, over 60 per cent of this water was extracted in five cases, over 53 per cent in two cases and about 45 per cent in the final instance. Not more than 16,000 pounds pressure per square inch was ever required, and it should be stated that very little solution (none in most cases) was secured above 10,000 pounds pressure per square inch, although, to be sure of uniform treatment, the final pressure used was in all cases 16,000 pounds.<sup>6</sup> In practically every instance, at least three-quarters of the soil solution was obtained before the gauge registered 20,000 pounds total pressure (6,370 pounds per square inch of piston surface). Another interesting fact is that, in almost all cases, the percentage of moisture in the soil after pressing was within less than one per cent of its calculated wilting coefficient. In other words, the amount of soil water removed by direct pressure was approximately the same as that which plants are able to secure when growing under proper conditions.

<sup>6</sup> Pressures up to 100,000 pounds were employed in a few cases, after the usual pressing but, from the fine sandy loam soils, no more solution was ever forced out. This was *not* the case with the other soil types. Very little moisture was expressed from clay loams until at least 15,000 pounds per square inch had been applied.



The so-called "unfree" or "combined" water of soils as determined by Bouyoucos (1) (that fraction which cannot be frozen) has been determined for these soils by Hoagland (7, p. 371), and is given for reference in the last column of the table. By comparison with data shown in column 3, we see that in some cases, the moisture content has been reduced by pressing almost to the point of "unfree water," while the average difference for all determinations is but a little over 3 per cent above the mean "unfree water" content.

*The analyses of the soil solutions*

About 500 cc. of soil solution were required for the several determinations made. As from 30 to 40 cc. of solution was obtained per single pressing (about 400 gm. of moist soil to the charge), from 15 to 20 pressings from each soil were usually necessary. With Press no. 2, each portion required about 30

TABLE 7  
*The chemical composition of the soil solutions*

SOIL NUMBER	PER- CENTAGE OF SOIL WATER EX- TRACTED	SPECIFIC RESIST- ANCE	RE- ACTION	TOTAL SOLU- BLE SOLIDS	INOR- GANIC SOLIDS	Ca	Mg	K	NO <sub>3</sub>	PO <sub>4</sub>	SO <sub>4</sub>
	<i>per cent</i>	<i>ohms</i>	<i>pH</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
3*	60.3	635.0	7.3						97		
7	65.4	454.4	6.9	1950	1110	270	62	42	389	2	173
8	52.5	457.6	7.0	2120	1210	223	65	67	549	2	251
9	44.8	480.6	7.0	1760	1010	223	43	33	212	1.5	177
10	63.5	377.6	7.1	3300	1500	355	97	81	487	2.5	170
11	61.2	211.2	6.9	4300	2490	452	154	108	761	5.5	293
12	63.4	600.0	7.0	1000	630	110	67	16	71	1.5	
14	52.7	475.1	6.9	1920	1090	208	55	82	566	1.8	148

\* Not completely analyzed.

minutes, so that an entire day's work was ordinarily necessary to secure the needed volume of liquid. The solutions were immediately taken to the laboratory, filtered through paper if turbid, separated into the aliquots required for the several determinations, and the evaporations started at once so as to avoid any possible bacterial alteration of the solutions. Calcium was determined volumetrically, and magnesium, gravimetrically, in 100 cc. aliquots, phosphates (21) in 200 cc. aliquots, potassium (21) in 100 cc. aliquots, while sulfates were gravimetrically determined on the residue from the inorganic solids portion. Nitrates were determined by the phenol-disulfonic-acid method on a 25 cc. aliquot. The conductivity measurements were made on the 200 cc. portions which were subsequently used for the phosphate determinations. Due to the usual presence of considerable amounts of nitrates, the hydrogen-ion concentration measurements were made colorimetrically on 8 or 10 cc. of the solutions. The results of these analyses appear in table 7.



The concentrations of the several ions have all been figured to parts per million of soil solution. Considerable silica and sodium, as well as iron, were noticed in several of the soil solutions during the course of the analyses. These were not quantitatively determined, except the iron in the case of soil solution 10. This solution carried 14 p.p.m. of dissolved iron (Fe). Slight precipitates of ferric hydroxide were noticed upon adding ammonium hydroxide in most of the solutions, prior to the calcium precipitation.

The specific resistance measurements are interesting in that they show the total ionic concentration of the soil solutions secured. Recalling that resistance decreases with increased concentration, we see that, with the exception of soil 7, a correlation is in all cases possible between the total dissolved solids as tabulated in column 5 and the resistances in ohms as shown in column 3. The order of decreasing concentration is as follows: soils 11, 10, 7, 8, 14, 9 and 12. By referring to Burd's (3) discussion of the relative fertilities of these same soils as shown by cropping tests we find the following classification: Good, 11, 8 and 14; medium, 10 and 7; poor, 9 and 12.

Using the freezing-point method of Bouyoucos, Hoagland (7) has calculated the concentration of total dissolved solids in the soil solutions of these soils under approximately optimum moisture conditions. The following table presents the averages of his results as secured periodically over a period of several months from the soils of the tank experiment, together with those directly determined on the soil solutions of the same soils by the writer.<sup>7</sup>

TABLE 8  
*Calculated and determined concentrations (dissolved solids) of soil solutions*

SOIL NUMBER	CALCULATED BY HOAGLAND FROM LOWERED FREEZING POINT		DIRECTLY DETERMINED ON BIN SOILS
	Fallowed	Cropped.	
	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
7	3666	1830	1950
8	3850	1700	2120
9	2250	1400	1760
10	3200	1750	3300
11	4200	1800	4300
14	3000	2100	1920

The results determined directly from the expressed solutions are in most cases much lower than those calculated from freezing point data on the fallowed soils but higher than those from the cropped soil. There are points of similarity, however. For instance, both methods show soil 11 to carry the solution of highest concentration while soil 9 gives the lowest results. It should

<sup>7</sup> While the samples for all of this series of determinations came from the same original lots of soil, those experimented upon by Hoagland had been subsequently cropped and otherwise differently treated from those used by the writer, which had been stored in bins for the past five years in an air-dried condition.

be recalled in making these comparisons that, while originally, each fallowed, cropped and bin soil was identical. differences in subsequent treatment have altered their amounts of readily soluble materials.

Column 4 of table 7 shows all of the soil solutions to be practically neutral in reaction. The hydrogen-ion concentration determinations were made by the colorimetric method.

The concentration of calcium ions is consistently high when compared with similar data for the more humid eastern soils as given by Morgan (14), using the oil-pressure method. The range found by the writer varies from 200 to 300 p.p.m. of soil solution, whereas for Michigan soils 100 to 200 p.p.m. is the rule. Concentration of magnesium ions in the soil solutions from the California soils studied, range from 60 to 100 p.p.m. of solution, while slightly higher results are reported by Morgan for humid soils. Potassium-ion concentrations are from two to three times as great in the solutions from western soils; while, as might be expected, the nitrate ion is a variable factor in both cases. The concentration of the phosphate ion is exceedingly low and shows but slight variations, either as between eastern and western soils or between the solutions from soil of different degrees of productivity (1, p. 305). The total range was from 1.5 to 3.5 p.p.m. of solution. Sulfates varied from about 150 to 300 p.p.m.

If the reacting values of the ions<sup>8</sup> are calculated, and the total weights of basic and acidic ions compared, there will be found to be a great preponderance of basic ions in all of the solutions reported. This is doubtless due to the fact that the  $\text{HCO}_3$  ions as well as the  $\text{Cl}$  and  $\text{SiO}_3$  ions were not determined and hence could not be used in these computations. That considerable quantities of calcium carbonate and bi-carbonate were present in these soils was shown by Stewart, and tests by the writer showed slight effervescence with  $\text{HCl}$  in one or two cases.

#### *Water-extraction studies*

Since an important part of this work was to be a quantitative comparison between the soil solution extracted by the direct pressure method and 1:5 water extracts of the same soils, portions were extracted with  $\text{CO}_2$ -free water and the resulting solutions analyzed for the  $\text{Ca}$ ,  $\text{Mg}$ ,  $\text{K}$ ,  $\text{NO}_3$ ,  $\text{PO}_4$  and  $\text{SO}_4$  ions.

The extracts were made by placing the equivalent of 400 gm. of dry soil in a clean, dry, acid bottle, adding sufficient water to effect the ratio of 1 part of soil to 5 of solvent, and shaking in an end-over-end shaking machine (10 r.p.m.) for exactly 1 hour. The solutions were allowed to settle and then filtered through Pasteur-Chamberland porcelain pressure filters rejecting the first 200 cc. On these perfectly clear solutions the determinations were made. The methods used were similar to those already described for the soil solution work, except that larger aliquots (400 to 600 cc.) were here found necessary.

<sup>8</sup> The valence divided by the atomic weight, or the ionic weight as the case may be.

Specific resistance determinations were also made on these extracts. Hydrogen-ion concentrations were determined on the soils themselves by the electrometric method.

The results secured are recorded in table 9, as parts per million of the soil extracts. To convert this data into parts per million of water-free soil, multiply by five.

TABLE 9  
*The chemical composition of the 1:5 water extracts*

SOIL NUMBER	SPECIFIC RESISTANCE	REACTION	Ca	Mg	K	NO <sub>3</sub>	PO <sub>4</sub>	SO <sub>4</sub>
	ohms	pH	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.
3	4672	7.4						
7	6197	7.3	16.6	4.1	5.4	13.2	1.8	13.0
8	6450	7.1	10.0	3.3	7.1	18.0	2.7	15.1
9	6963	7.2	10.8	2.7	4.2	9.0	0.8	9.3
10	4992	6.5	17.5	5.7	11.2	44.0*	2.5	15.0
11	3680	7.1	15.5	6.0	12.3	24.6	10.1	16.0
12	8730	6.9	6.2	5.5	3.6	2.1	0.8	12.5
14	6075	7.0	9.0	5.7	13.9	22.0	1.9	11.0

\* This figure is apparently too high.

The specific resistances of these soil extracts varied between 3680 ohms and 8730 ohms. Those found by Stewart (21) to be of high productivity invariably showed a lower resistance and hence a higher soluble salt content than those which produced the poorer crops. The hydrogen-ion determinations showed the soils to be about neutral, with the exception of soil 10 which was slightly acid and soils 7 and 3 which were slightly alkaline. Of the cations determined, calcium and potassium were found to vary most as between the different soils; the former from 6.2 to 17.5 p.p.m., the latter from 3.6 to 13.9 p.p.m. of solution. Magnesium was present in smaller quantities and varied but slightly (2.7 to 5.7 p.p.m.). The phosphate-ion concentrations were less constant than had been anticipated from the recognized low solubility of soil phosphates. They varied from less than 1 p.p.m. to over 10 p.p.m. in the case of soil 11. However, with this one exceptionally high concentration, the differences were less (from a little below 1 p.p.m. to about 2.5 p.p.m.). As would be expected, nitrates were the most divergent, varying from 2 to over 20 p.p.m. The sulphate ion was the most constant of the anions. Its range was 9 to 16 p.p.m.

#### *Comparisons between soil solutions and their aqueous extracts*

Several theoretical discussions may be found in the more recent literature as to the permissibility of drawing conclusions concerning the approximate quantitative concentrations of true soil solutions from data secured by extracting these soils with pure water and comparing such results with cryoscopic determinations. While it is doubtless a fact that those substances present

in the true soil solution form a certain definite fraction of those dissolved in a 1:5 pure water extract of that same soil, we are hardly able to calculate just how great a part of the solutes in such an extract formerly belonged to the true soil solution and just how much has been subsequently dissolved by the greatly diluted solution formed by the addition of so great an excess of pure water. Mitscherlich (13), and more recently Hoagland (7) (8), have attempted to compute from such extraction data the actual soil solution concentration. That many difficulties arise in such calculations have been fully realized by these investigators. For instance, Hoagland (7, p. 390) writes:

In the first place, it is not safe to assume that a curve based on one range of extractions can accurately be extended to cover another range of extractions. Indeed, the experimental data indicate that with the smaller proportions of water the curves may change their direction very appreciably and it is unfortunately impracticable to obtain extracts for analysis in those concentrations which correspond to optimum moisture conditions. Another limiting factor previously neglected, has been described by Stewart. This concerns the differential effect of the solvent. The actual solvent in any case is not pure water, but pure water plus the solids already dissolved in the soil solution, and these vary enormously with changing conditions, even in the same soil. It is quite obvious that this factor would modify any calculations of the concentration of the soil solution based on water extracts. . . . If we should contrast the concentration of the soil solution, calculated from the extracts to the total moisture of the soil, with the concentrations shown by the freezing-point method, there would be a general similarity of magnitude. Logically, however, a comparison is much more justifiable when the extracts are calculated not to the total soil water, but to the "free water," in the sense meant by Bouyoucos. It is then apparent that the concentration of the soil solution calculated by the extraction method is from two to five times that indicated by the depressions of the freezing point.

Hoagland, et al. (8) also remark:

The value of the determination made by the water-extraction method rests primarily on the assumption that a logical relationship exists between water extracts and the soil solution. . . . When a 1-to-5 extract of soil is made with distilled water, the quantity of total solids is from 1.5 to 5 times that present in the soil solution, as calculated by the freezing-point method.

That Hoagland is justified in stating that comparative data of some value may be obtained by the water-extraction procedure is generally borne out by facts hereafter presented, although results that more nearly reflect the concentration of the true soil solution might be obtained by making the freezing-point determinations at or above the soil's saturation point (16, p. 229) and discarding the "unfree water" idea entirely in performing the calculations.

In order that valid comparisons may be drawn between the concentration and composition of the soil solutions and the water extracts of the same soils, it is obviously necessary to arrange the data as given in tables 7 and 9 so that they are as nearly as possible comparable. In order to gain this end, the writer has calculated all data to the basis of water-free soil; i.e., the data have been figured in such a way that the solutes in each cubic centimeter of soil solution or of water extract are the amounts dissolved from a definite weight of water-

free soil. A moment's reflection will show that there are two different ways in which these data may be calculated and compared. The first would assume that in all soils a part of the soil solution is either physically or chemically combined and plays no active part as a true solvent (the "unfree-water" idea of Bouyoucos), hence it should be subtracted from the "total moisture" in the case of each soil before calculating the concentration of the soil solution in terms of "parts per million of water-free soil." The second viewpoint would assume that all of the water in soils acts as a true solvent and that none of it belongs to the so-called "unfree" class. In the light of recent work grave doubts exist in the minds of many soils scientists as to whether any such thing as "unfree water"—at least in any quantity—really exists in soils. To the writer, the presence of large amounts of "unfree water" seems highly specula-

TABLE 10

*Pressure-extracted soil solutions, with "unfree water" subtracted, compared with water-extracts of the same soils (parts per million of water-free soil)*

SOIL NUMBER	CALCIUM		MAGNESIUM		POTASSIUM		NITRATE		PHOSPHATE		SULFATE	
	Soil solution	Water extract	Soil solution	Water extract	Soil solu- tion	Water extract	Soil solu- tion	Water extract	Soil solu- tion	Water extract	Soil solu- tion	Water extract
	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.
7	35	83	8	20	7	27	51	66	0.3	9	23	65
8	32	50	9	16	9	35	78	90	0.4	14	35	76
9	26	54	5	14	4	21	25	45	0.2	4	21	46
10	53	88	15	29	12	56	73	220*	0.4	13	26	74
11	54	78	18	29	13	62	90	123	0.7	50	35	79
12	19	31	12	27	3	18	13	11	0.3	4		63
14	30	44	8	29	13	70	82	110	0.4	9	22	55
Average..	35	62	11	23	8.5	41	59	95	0.4	15	27	65

\* This figure may be in error.

tive. The data has been figured both ways (see tables 10 and 11) and briefly discussed from each standpoint. The reader may choose as to the merits of each.

Table 10 presents the comparative results, the "unfree water" (see table 6) being taken into account and subtracted.<sup>9</sup> Figured in this way, approximately twice as much of each of the important nutrient ions, except potassium and phosphate, are found to be extracted by an excess of solvent as was dissolved in the "free water" of the soil solutions when the latter were secured from soils at near their optimum moisture content for plant production. The averages given at the bottom of table 10 show that in the case of calcium, 35 p.p.m. are present in the soil solutions, while 62 p.p.m. are removed in the 1:5 water extracts. In the case of magnesium the ratio is 11 to 23; for nitrate,

<sup>9</sup> (Total moisture—"unfree water")  $\times$  concentrations shown in table 7 = p. p. m. of dry soil.

59 to 95; and for sulfate, 27 to 65. It is interesting in this connection to note that Hoagland, discussing results secured by the cryoscopic method on these same soils, writes (7, p. 391):

If we use the freezing point depressions as a basis, it appears that from 0.01 to 0.03 gm. of total solids is in solution for each 100 gm. of moist soil, while the total solids obtained by the 1-5 extractions vary from 0.02 to 0.06 gm. per 100 gm. of soil. This means that not more than 50 per cent could have originally been present in the soil solution. . . . but usually the extracts would still give somewhat higher results.

As stated above, the calcium, magnesium, nitrate and sulfate comparisons (and these ions probably make up 85 to 90 per cent of the total inorganic solids) are in close agreement with these statements. Unfortunately total solids were not determined on the 1:5 water extracts, so a direct comparison with Hoagland's data is not possible.

The amounts of potassium dissolved by the excess of solvent, on the other hand, are in all cases about five times as great as appear to be originally present in the soil solutions, the average ratio being 8.5 to 41 p.p.m. of dry soil. The reason for these greater amounts of potassium in the 1:5 extracts may possibly be found in the fact that these arid soils, potentially high in this element in fairly available forms, readily furnish to the excess of solvent the additional potassium required to approach equilibrium under the altered conditions.<sup>10</sup>

Cameron and Bell (5) and Schreiner and Failyer (20) some years ago noted the fact that potassium (and phosphorus) behaved differently from the other soil elements in so far as solution and reabsorption phenomena were concerned. By an ingenious electrical apparatus for the continuous extraction of the water-soluble inorganic constituents of soils, these investigators showed the potassium of soil minerals to be especially soluble in pure water. By means of percolators, using both soil extracts and solutions of pure potassium salts, they were also able to demonstrate the absorption of large quantities of the potassium ion, and show that this absorptive power of soils tends largely to obscure the solvent effects. The latter investigators state:

"The constancy of the removal of the absorbed potassium by water is even more striking than in the case of the phosphate and the conclusion that the true soil moisture is largely dependent on the absorptive power of the soil is well sustained by these results. The absorbed potassium is continually diffusing, and becoming directly accessible to plants."

It would appear from the above data that lesser amounts of the potassium ion are present in true soil solutions than was formerly surmised, but that in highly productive soils, the ability rapidly to renew and constantly to maintain adequate concentrations of this element obtains.

The comparative data shown for the phosphate ion are of interest. The complexity of phosphate fertilization has long been recognized. It is well known that a large excess of phosphates is necessary to maintain adequate concentrations of this element in most soils.

<sup>10</sup> We are dealing here with solution and redistribution of the K-ion between soil and solvent. The colloidal surface exposed for reabsorption in these arid soils is probably small.



Schloessing, Schreiner and Failyer and others have shown that solutions obtained by successive extractions of a soil with pure water have a phosphate-ion concentration which, after one or two extractions, is practically constant, and that, when the same soil has been allowed to absorb large quantities of soluble phosphate, subsequent to the first and second leachings, the concentrations thereafter yielded are constant and practically those given by the original soil with a far less phosphate content. Schreiner and Failyer (20) thus conclude: "that the concentration of the phosphate in the soil solution is practically constant whether the soil contains a large or a small quantity of total phosphate, and that it is the absorptive power of the soil which controls this concentration in the free soil moisture. It follows that with change in the absorptive power of the soil, the concentration of the phosphate in the soil moisture would also change."

Cameron and Bell (5) have studied the effects of water and aqueous solutions upon soil phosphates and they show that an increase in the salt concentration of the solvent tends to depress phosphate solubility. Especially do fairly concentrated solutions of many of the lime salts notably decrease the amounts of phosphoric acid going into solution.

TABLE 11

*Soil solutions and water extracts of the same soils directly compared on the basis of parts per million of water-free soil*

SOIL NUMBER	CALCIUM		MAGNESIUM		POTASSIUM		NITRATE		PHOSPHATE		SULFATE	
	Soil solution	Water extract	Soil solution	Water extract	Soil solution	Water extract	Soil solution	Water extract	Soil solution	Water extract	Soil solution	Water extract
	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.
7	52	83	12	20	8	27	74	66	0.4	9	33	65
8	41	50	12	16	12	35	100	90	0.4	14	46	76
9	40	54	8	14	6	21	38	45	0.3	4	31	46
10	82	88	23	29	19	56	112*	220*	0.6	13	39	74
11	80	78	27	29	20	62	135	123	1.0	50	52	79
12	25	31	15	27	4	18	15	11	0.3	4		63
14	46	44	12	29	18	70	124	110	0.4	9	33	55
Average..	52	62	16	23	12	41	81	76	0.5	15	39	65

\* One or the other of these figures is apparently in error. They have been omitted from the averages.

These facts should be borne in mind as we view the data recorded in table 10. An average of about 35 times as much phosphate ion was removed from the soils by extracting with pure water, in the proportion of 1 part of soil to 5 of water, as was present in the soil solutions expelled by direct pressure; i.e., less than one-half of one part per million (of dry soil) was present in the soil solutions, whereas about 15 p.p.m. was removed on an average with the excess of solvent. Referring to table 7 we see that the concentration of phosphate ion in the soil solutions themselves varied from 1.5 to 2.5 p.p.m. in most cases, while table 9 shows that the concentrations of the 1:5 extracts were not far from the same in p.p.m. of extract. Similar magnitudes are recorded by several investigators for the solubilities of natural tricalcium phosphate and for other soil phosphates in pure water.

Table 11 presents the same comparative data calculated directly to the dry-soil basis, on the assumption that there is no such thing as "unfree water,"



and that the moisture expressed simply represents fractions of uniform soil solutions, all portions of which function as true solvents.

A study of table 11 indicates that the average amounts of magnesium, calcium and nitrate ions removed by the great excess of solvent are but slightly greater than those removed in the true soil solutions.

These results are in direct accord with the recent findings of Parker (16), who shows that the concentrations of nitrate-nitrogen and of total soluble salts (figured on dry soil) are approximately the same, whether true soil solutions secured by alcohol displacement, or 1:5 water extracts are analyzed. Hoagland, et al. (8) also give data which show but slight increases in the amounts of calcium, magnesium and nitrate obtained in 1:5 water extracts over those amounts secured by 1:1 extracts. They state (8, p. 388),

"It is plausible to assume that this diluted soil solution would bring into solution principally either 'absorbed' salts or easily soluble chemical compounds, originally derived from the more resistant minerals. . . . This latter fraction of the soil extract would ordinarily form only a small portion of the total dissolved material."

Much doubt, it would seem to the writer, is cast on the "unfree-water" idea by the fact that only about one-half of the nitrate ion is shown to be dissolved in the soil solutions of table 10 (after subtracting the "unfree water"), while numerous data are extant showing that absorption of nitrates by soils is practically a negative quantity. Potassium ion stands in the ratio of about 1 in the soil solutions to  $3\frac{1}{2}$  in the extracts, while phosphate ion differs but slightly from the values shown in table 10. A possible explanation for the peculiar conduct of these two ions has already been advanced: i.e., the adsorbed potassium of soils being readily dissolved in an excess of solvent, and the sparingly soluble phosphates readily forming a saturated solution as the proportion of solvent is increased. Hoagland (8) has reported similar data.

The concentration of the sulfate ion is also greater in the water-extracts, the ratio being about 1 to 1.7. Any explanation of this fact would be purely speculative. It should be remembered, however, that the amounts of the several ions found by the analysis of these aqueous solutions are the resultants established between the processes of solution on the one hand and those of reabsorption on the other; i.e., they represent an approximate distribution equilibrium of solute between the soil and the solvent (17).

#### SUMMARY

The importance of more extended knowledge concerning the concentration and composition of the soil solution as it exists in soils at ordinary moisture contents is admitted by all students of our science. The present paper describes a direct-pressure method for securing sufficient quantities of this liquid phase of soils for analytical purposes. It presents a quantitative chemical study of such solutions, and finally, it compares these results with similar data from the same soils, obtained by the 1:5 water extraction method.

A somewhat detailed description of the apparatus is given. This consisted of properly constructed presses for holding the soils, while heavy testing machines supplied the required pressures.

The soils employed were fine sandy loams and came from different parts of California. Portions of these same soils had previously been used by Hoagland and Stewart in vegetation and soil-extract work (see references).

Preliminary experiments demonstrated that the pressures used had no measurable effect on soil solubility as shown by various tests made on different fractions of soil solution, secured at increasing pressures; also that there was no appreciable fining or abrasion of the soil particles due to the pressures applied.

From eight soils, moistened to but 50 per cent of their total moisture-holding capacities, over 60 per cent of the water was extracted in five cases, over 52 per cent in two cases, and about 45 per cent in the final instance. Very little solution was secured from any of these soils above 10,000 pounds pressure per square inch.

Analytical data, showing the chemical composition of the soil solutions, are submitted. This work involved determinations of Ca, Mg, K,  $\text{NO}_3$ ,  $\text{PO}_4$  and  $\text{SO}_4$  ions, besides total solids, conductivity measurements and hydrogen-ion determinations.

Similar data are given for 1:5 water extracts of the same soils.

A comparison between soil solutions and 1:5 aqueous extracts is made, discussing the results from two points of view: First, subtracting the so-called "unfree water" in computing the concentrations of the several ions found in the soil solutions; and second, considering that all of the water in soils is free to act as a true solvent. In the light of the data submitted, the latter seems more tenable to the writer.

The important facts brought out by the above comparisons may be briefly summarized as follows: Where the "unfree water" is subtracted, about twice as much calcium, magnesium, nitrate and sulfate is removed in 1:5 water extracts as is found in the soil solutions. The potassium-ion determinations show the extracts to carry, on an average, five times as much as is dissolved in the soil solutions. In the case of phosphates, approximately 35 times as much is removed by the excess of solvent. Where we do not subtract "unfree water," but consider that all of the soil moisture is capable of uniformly dissolving soil materials, we find that the average amounts of calcium, magnesium and nitrate dissolved and removed are practically equivalent by the two methods, while about 3.5 times as much potassium and 1.7 times as much sulfate are removed by the 1:5 extraction method. The phosphate ion is still dissolved in large quantities (over 30 times as much) by the excess of solvent.

A definite relationship is shown to exist between the conductivity measurements of soil solutions and of 1:5 water extracts of the same soils. These comparative data are also in close agreement with the known productivity of the several soils examined.

All of the soil solutions are practically neutral, while the hydrogen-ion concentrations of the soils themselves vary from pH 6.5 to 7.4.

Brief mention is made of certain experiments wherein the oil-pressure method was found to be of questionable value (at least with Hawaiian soils) for securing satisfactory quantities of a uniform soil solution.

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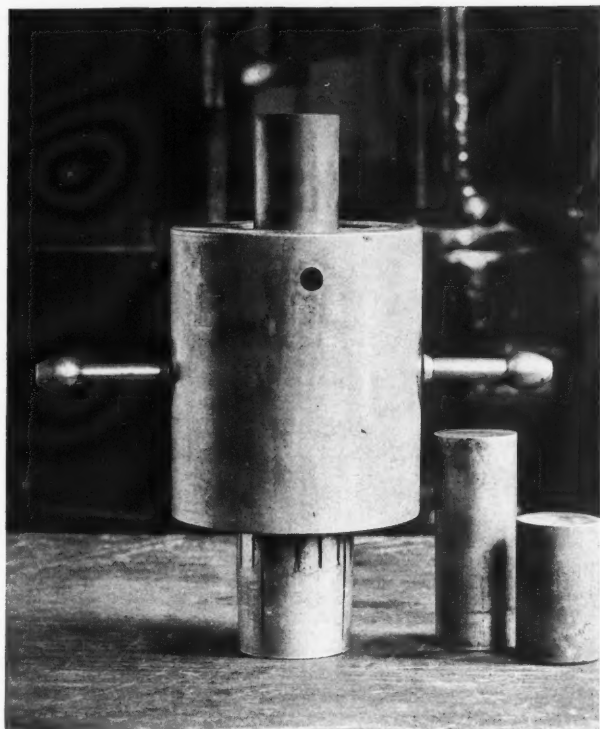


FIG. 1. PRESS NO. 2, SIDE VIEW

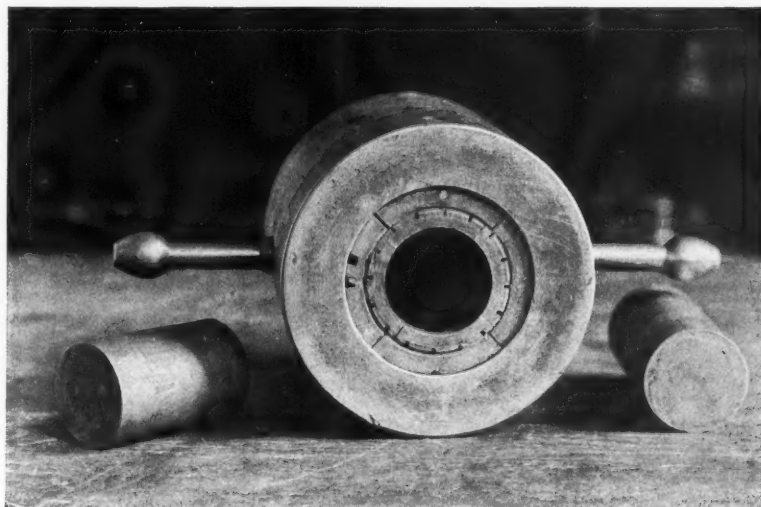
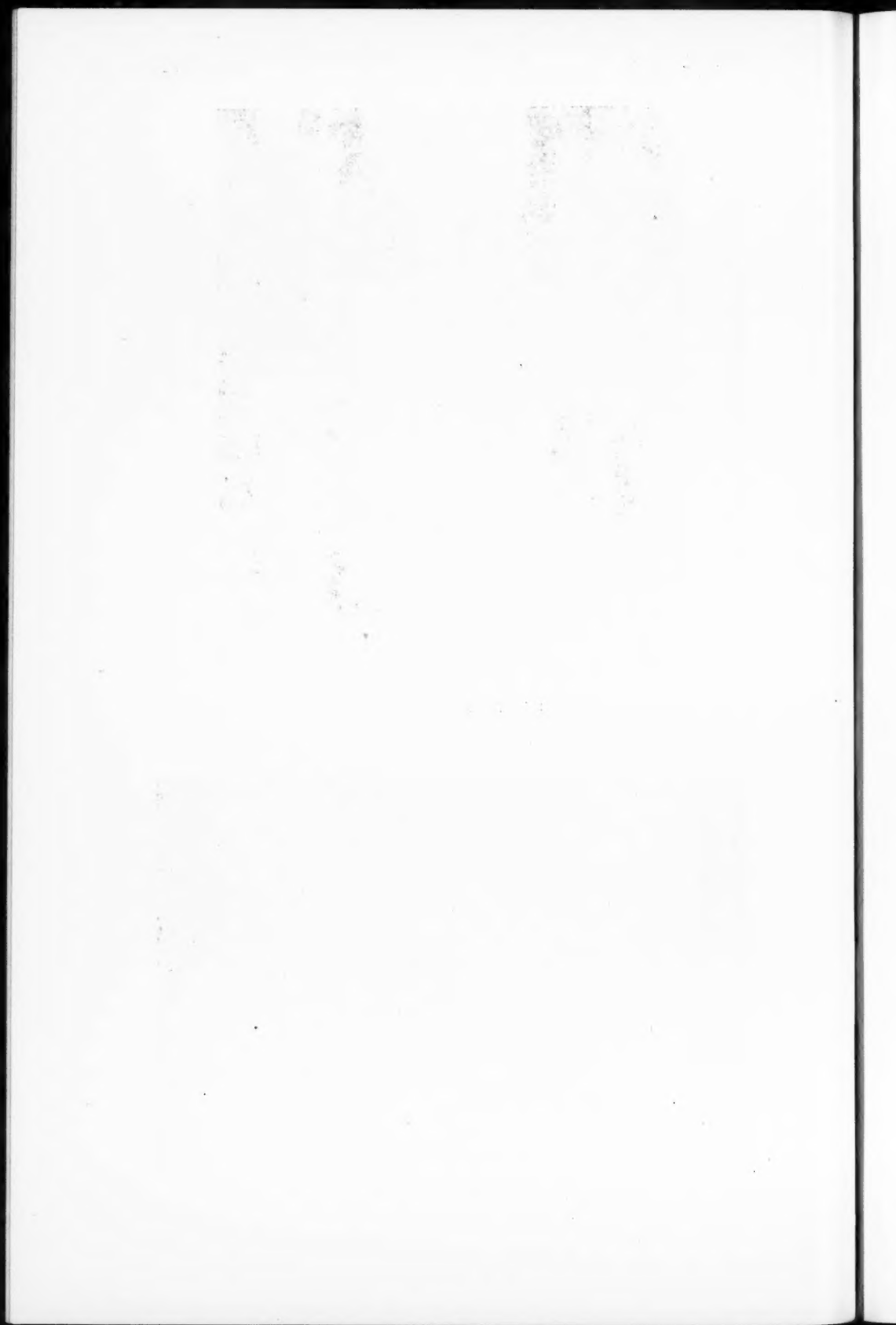


FIG. 2. PRESS NO. 2, END VIEW



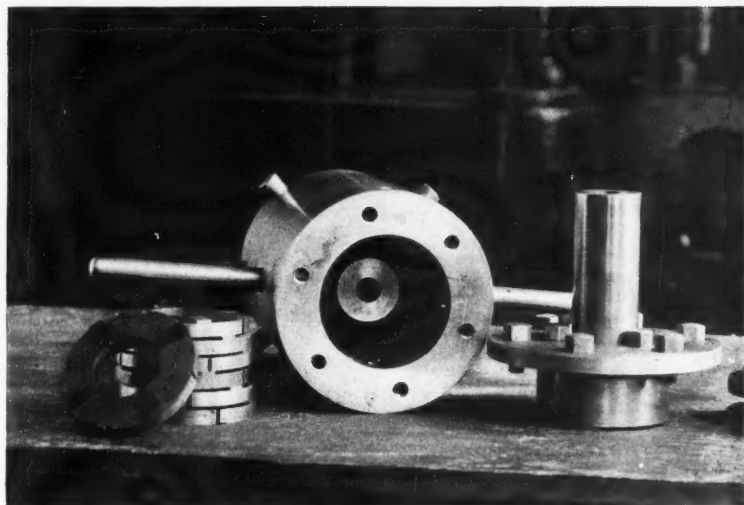


FIG. 1. PRESS NO. 3, SHOWN IN DETAIL

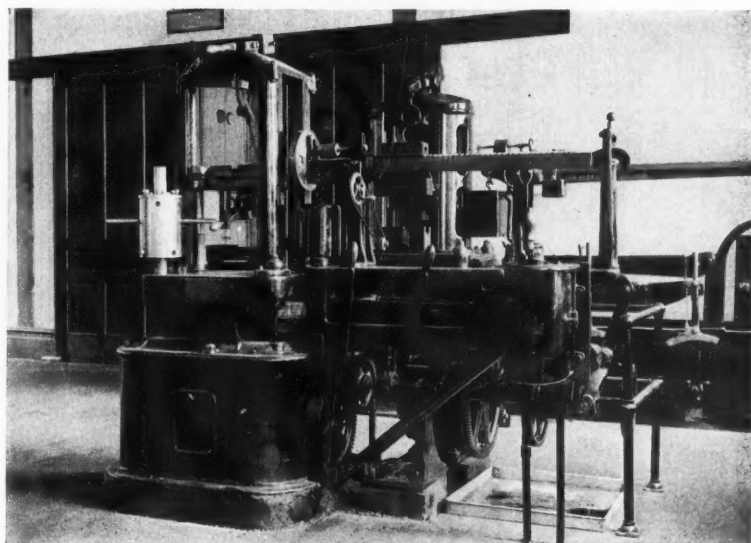
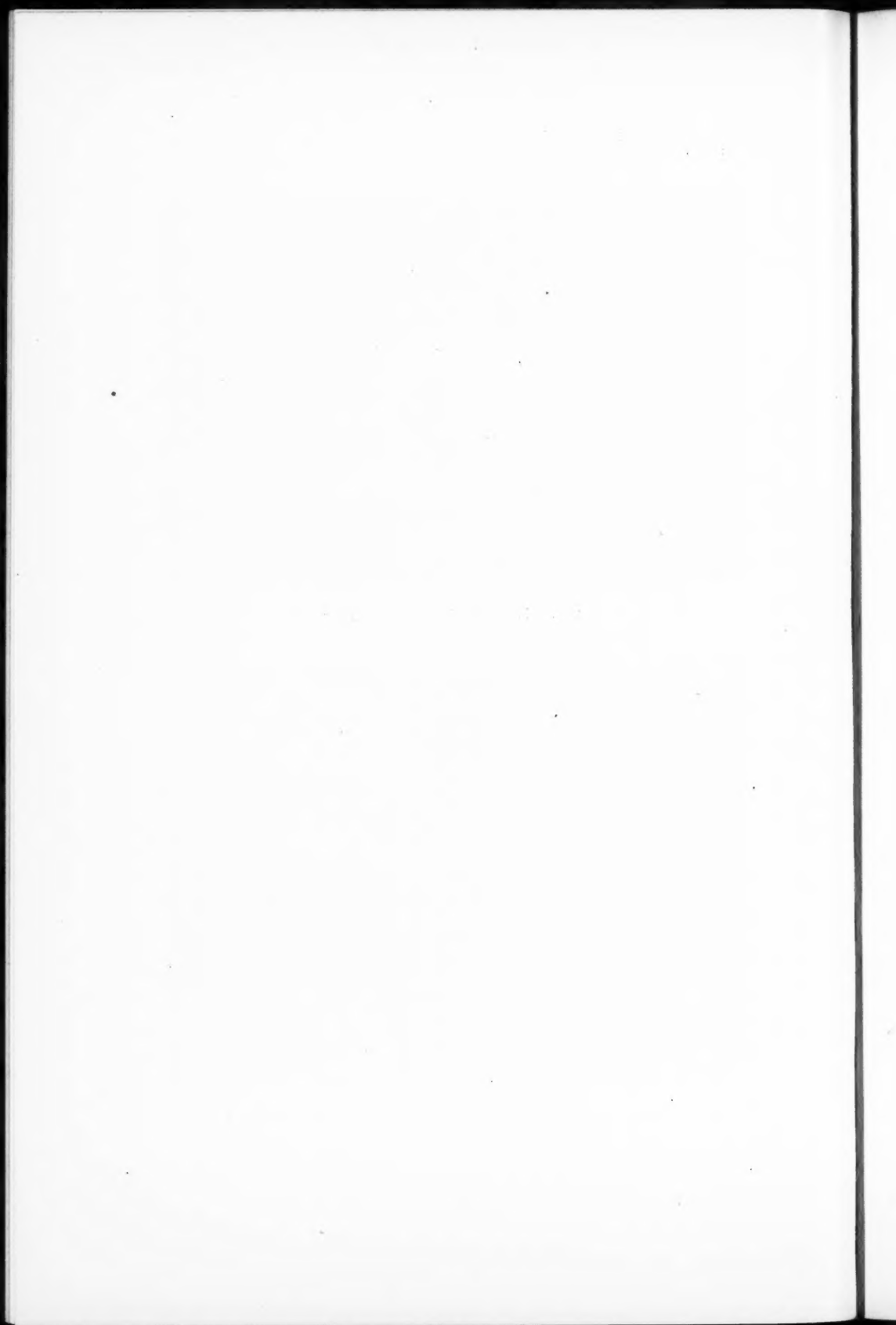


FIG. 2. PRESS NO. 3, ASSEMBLED AND RESTING ON TABLE OF TESTING MACHINE





## A NOTE ON OXIDATION OF SULFUR IN OREGON SOILS<sup>1</sup>

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As outlined elsewhere (1,2) the sulfur transformations in soils consists in oxidation of sulfides, sulfites and elementary sulfur to sulfates. Since sulfides have to go through the sulfur stage, a study of sulfur oxidation naturally includes sulfide oxidations. The soil is the medium of these reactions. Their successful accomplishment depends, therefore, upon the fitness of the soil for the proper functioning of the organisms. Since soils in close proximity may vary in composition, texture, drainage, temperature, reaction, etc.; these conditions determine for each soil a certain capacity to oxidize sulfur. Some of these features have been studied before, as may be seen from the publications referred to (1,2), but the relation of capacity of soils to adjust their reaction to changes in intensity of acidity due to sulfur oxidation, the capacity to absorb or adsorb the acids formed, the differences in oxidation from inoculated and uninoculated has not been dealt anywhere.

The experiments reported below were undertaken to investigate these features on a series of 8 Oregon soils. These soils are known for their response to sulfur treatments with consequent increases in alfalfa yields, the increases varying from 35 to 500 per cent.

The soils here described were obtained from the Oregon Experiment Station through the courtesy of Dr. Reimer, who describes these soils in Bulletin 163 of the Oregon Agricultural Experiment Station (4) in connection with the use of sulfur as a fertilizer for alfalfa:

1. Agate gravelly loam. A red, clay loam underlaid with an impervious hard pan. The surface soil contains 0.024 per cent of sulfur. Sulfur applications proved very beneficial.
2. Tolo loam. Typical red, foothill clay loam, underlaid with a tenacious yellow clay. Sulfur applications was slightly beneficial.
3. Medford loam. A deep brown fertile silt loam; the soil contains .036 per cent of sulfur; best alfalfa soil in Rogue River Valley; no benefits from sulfur applications.
4. Antelope clay adobe. Heavy black adobe soil of a very sticky nature, deep and well drained; the sulfur content is 0.02 per cent. Sulfur application increased the yield as high as 1000 per cent.
5. Phoenix clay adobe. Heaviest adobe, contains 63 per cent of clay and 21 per cent of silt; the sulfur content is 0.021 per cent; iron sulfate had no effect on yields.

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<sup>1</sup>Paper No. 83 of the Journal Series New Jersey Agricultural Experiment Station, Department of Soil Chemistry and Bacteriology. This paper will appear in *RUTGERS COLLEGE STUDIES*, vol. 1.

6. Barren coarse sand. Coarse granite of considerable depth; the sulfur content is 0.028 per cent; sulfur applications proved beneficial.

7. Anderson clay loam. Deep, black fertile clay loam of alluvial origin. No response to sulfur applications.

8. Salem clay loam. Deep fertile clay loam, contains 21 per cent of clay and 40 per cent of silt; the sulfur content is 0.027 per cent; sulfur applications increased the yield as high as 500 per cent.

#### EXPERIMENT 1

One-hundred-gram portions of these soils were distributed in tumblers, 100 mgm. of sulfur<sup>2</sup> was added to each one and sufficient water to make up the moisture optimum for each particular soil. Two series were prepared in one inoculated sulfur was used, in the other uninoculated.<sup>3</sup> Table 1 gives the results of the experiment.

TABLE 1  
*Course of reaction and amount of sulfur oxidized*  
Sulfur application, 2000 pounds per acre

SOIL NUMBER	RE- ACTION OF ORIGI- NAL SOIL	INOCULATED SULFUR				UNINOCULATED SULFUR			
		After 15 days' incubation		After 32 days' incubation		After 15 days' incubation		After 32 days' incubation	
		Reac- tion	Sulfur oxidized in 100 gm. of soil	Reac- tion	Sulfur oxidized in 100 gm. of soil	Reac- tion	Sulfur oxidized in 100 gm. of soil	Reac- tion	Sulfur oxidized in 100 gm. of soil
		pH	mgm.	pH	mgm.	pH	mgm.	pH	mgm.
1	6.2	6.2	10.39	5.1	43.95	6.2	6.01	5.2	30.09
2	6.2	6.0	37.98	5.8	58.25	6.0	32.73	5.8	60.99
3	6.2	6.0	23.68	5.2	61.52			5.2	56.06
4	6.4	6.0	8.48	5.2	41.39	6.4	8.2	5.4	31.17
5	6.4	6.0	24.61	5.8	44.2	6.4	5.47	6.0	38.77
6	6.0	5.2	33.15	4.4	54.75	6.0	23.85	4.4	56.94
7	6.2	5.4	34.74	5.4	64.26	5.8	31.18	5.6	43.33
8	6.4	6.0	19.14	5.4	56.83	6.0	22.7	5.2	63.18

The first striking feature of the data is the specificity of each soil as a medium for the sulfur oxidizing flora, i.e., the inherent sulfur-oxidizing capacity of the soil. It will be noticed that soil 4, after 15 and 32 days of incubation, oxidized less sulfur than any other soil. The next lowest in sulfur oxidizing capacity was soil 1. An examination of the physical character of these two soils will show that they are heavy in texture and consequently not well aerated. This condition, is indispensable for efficient sulfur oxidation. These soils, however as reported by Reimer and Tartar (4), have responded favorably to

<sup>2</sup> The sulfur added was calculated to be equivalent to 2000 pounds per acre of 2,000,000 pounds of soil.

<sup>3</sup> Through an error, the uninoculated soils were stirred with the same spatulae as the inoculated soils on the tenth day of incubation. Due to lack of material the experiment could not be repeated at this point.

sulfur treatment, with increases in crop production as high as 1000 per cent. Reimer was fully justified in recommending that the sulfur be applied far in advance of the growing season. Such a practice develops an active sulfur oxidizing flora which has to adjust itself to the adverse conditions of aeration. In speaking of sulfur as a fertilizer it has been mentioned that as yet the economy of sulfur metabolism by plants is not established. It is possible that large quantities of sulfates have to come into immediate contact with the roots before they can absorb the little sulfur the plant needs. From this standpoint, it is desirable to get as active oxidation as possible. The abundance of sulfates formed in the advanced periods of incubation will suffice for both leaching and crop uses. It is of interest to note that after 15 days of incubation the soils which did not respond so well to sulfur applications oxidized more sulfur than those that did benefit by its application. This was also true after 32 days of incubation. The only explanation that may be offered is that the soils not deficient in sulfur are perhaps in a better physical condition, as it may be inferred from the descriptions.

Another interesting feature is the capacity of these particular soils to neutralize, absorb and adsorb the acid formed. The buffer content of these soils seems to be fairly high. Especially is this true with the heavy soils. The record of the hydrogen-ion concentration measurements may serve as an index of the buffers present. It will be noticed that after 15 days of incubation the change in the pH values was only slight, although as high as 37.98 per cent of the sulfur was oxidized in soil 2. Since the application of sulfur was on the basis of 2000 pounds per acre it is clear that some soils will tolerate and benefit by unusually large applications of sulfur and not be injured even if there is a sufficient balance of this essential element in the particular soil. Soil 3 may serve as an illustration. According to Reimer and Tartar (4), this is one of the best alfalfa soils in Rogue River Valley. It is well supplied with sulfur in the proper form and sulfur applications did not increase the yield of alfalfa. But data show that in 15 days 23.68 per cent or 473 pounds of sulfur, was oxidized and still the reaction changed but slightly. Soil 7 oxidized close to 700 pounds of sulfur per acre in 15 days, but its buffer power is not as high as that of soil 3 and the reaction went down to a pH 5.4. This would indicate that for this soil a 700 pound application would be somewhat too much; from the pH values and the amount of sulfur oxidized one may easily predict the amount of sulfur it is safe to apply to any of the Oregon soil studied. The same criterion may be applied to every soil that is poor in sulfur. Soil 6 was a sandy soil having a very little buffering effect and naturally showed acidity at high applications of sulfur, although it did respond to small applications of sulfur as pointed out by Reimer. After 15 days it oxidized over 660 pounds of sulfur and the pH was 5.2, which is not a favorable reaction for the best growth of alfalfa. In such cases a heavy application of sulfur will show harmful effects, although a judicious application would undoubtedly be beneficial, as in the case of soil 6.

The third feature of this experiment is the difference in the speed of oxidation of sulfur in the inoculated and uninoculated soils. As pointed out the experiment could not be carried out as it was planned: the uninoculated soils were subject to inoculation after ten days. Still the differences are striking. In most cases the inoculate tumblers showed greater sulfur oxidation. Of especial interest is soil 5, the inoculated series of this soil oxidized in the first 15 days nearly five times as much sulfur as the uninoculated. The practical inference is that inoculated sulfur may be applied later and thus prevent losses by leaching. Moreover smaller amounts may be applied. This corroborates the results of Martin (3). It may be of interest to note that after a more prolonged incubation period nearly all the sulfur was oxidized and the reaction of the first five soils did not go below pH 5.0; soils 4 and 5 had a pH 5.4. This indicates the enormous capacity of these soils to oxidize sulfur and still maintain a reaction which will not inhibit growth, even of alfalfa.

TABLE 2  
*Course of reaction and amount of sulfur oxidized*  
Sulfur application, 250 pounds

SOIL NUMBER	PERIOD OF INCUBATION				
	15 days	30 days	45 days	60 days	
				Reaction	Sulfur oxidized
	pH	pH	pH	pH	per cent
1	6.2	6.0	6.0	6.0	72.5
2	6.2	6.2	6.0	6.2	81.6
3	6.2	6.0	6.2	6.0	84.2
4	6.2	6.2	6.2	6.0	71.4
5	6.4	6.2	6.2	6.2	74.9
6	5.8	5.6	5.6	5.3	86.3
7	6.0	5.8	5.8	5.8	87.2
8	6.2	6.0	6.0	6.0	82.3

#### EXPERIMENT 2

To further test the buffer capacity of these soils, the following experiment was carried out. The same procedure was used as in the first experiment. Only inoculated sulfur was used in this experiment. Sulfur was applied at the rate of 250 pounds per acre. Table 2 of the pH values shows that after a period of 60 days practically no change in the hydrogen-ion concentration took place. Every soil except soil 6 accommodated this amount very much to its advantage and enriched its sulfur resources. To see if the sulfur was oxidized, sulfates were determined after 60 days incubation and 70 to 80 per cent of the sulfur appeared as sulfates. Some sulfur was perhaps adsorbed as sulfates or in some other form. The data given in table 2 show that more than 250 pounds of sulfur may be applied to the soils studied without imparting a reaction inhibitory to the successful growth of alfalfa.

## SUMMARY

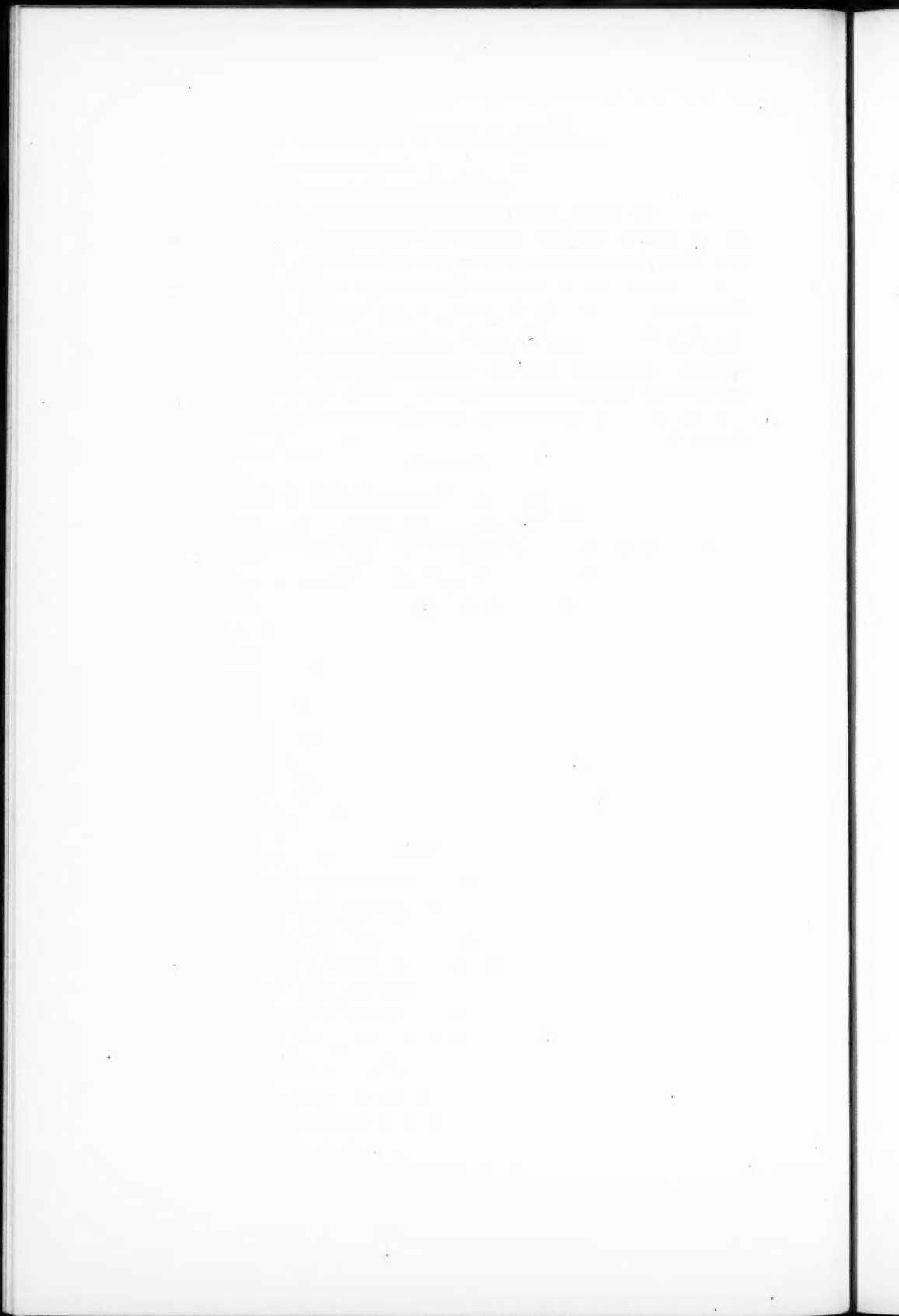
1. The sulfur oxidizing capacity of 8 Oregon soils was investigated. It was apparent that the soils of a low sulfur oxidizing capacity should receive the sulfur application in advance of the growing season.

2. The buffer action of these soils was measured by the changes in the hydrogen-ion concentration of the soil extract. It was found that most of the soils investigated did not materially change in reaction after having oxidized most of the 250 pounds of sulfur used, thus indicating that elemental sulfur may be applied as a fertilizer to these soils without danger of injuring crop production due to the acidity of sulfuric acid formed.

3. Comparisons of inoculated and uninoculated sulfur show that the former is more effective.

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## THE POTENTIAL ACIDITY OF SOILS

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Since Bjerrum (5) in his first two papers in a series on the causes of actual and potential<sup>2</sup> acidity of soils pointed out the great theoretical value of the knowledge of these properties, very few have worked on this subject.

The author, when investigating these soil characters, especially on some Oriental soils (1, 3, 4) found results which may be of both theoretical and practical value.

Chiefly, there are two different methods for measuring hydrogen-ion concentration, viz., electrometric and colorimetric. All measurements in this work are made according to the colorimetric method as modified by Gillespie (8). The accuracy of this method to the first decimal is quite sufficient for soil investigations where the deviations are so great, and it is so convenient that it can be used under conditions where no laboratory equipment is available.

The hydrogen-ion concentration was measured in soil extract made up as follows:

Ten grams natural moist soil were shaken with 50 gm. distilled water and then left to settle. The next day the extract was filtered and the pH value of the filtrate was determined. By this method there was introduced a source of error, viz., the probable change in the pH value of the soil solution when diluted. Sharp and Hoagland (14), however, give experimental data for the correctness of this method when not too large amounts of water are used.

The potential acidity in the following experiments was measured as follows:

In a series of flasks, usually nine, 5.00 gm. soil was introduced into each and then 10, 5, 2 and 1 cc. of about 0.1 *N* acid, or the same amounts of alkali was added, except in the case of the check, and the solution made up to 20 cc. with distilled water. The flasks were then corked, shaken for a time and left to settle. The whole procedure takes one day. After filtering, the pH values were determined colorimetrically in the filtrate. The amount of acid or alkali added is calculated in cc. of 0.1 *N* solution per gram of dried soil 100° C.

Sometimes stored soils have been used for hydrogen-ion concentration investigations and in order to determine the influence of drying on both the actual and potential acidity, the following experiment was carried out.

<sup>1</sup> Most of the work reported here has been carried out in the soils and bacteriology laboratory of the University of California. The author wishes to take this opportunity to thank Professors C. B. Lipman, W. F. Gericke, A. R. Davis, and D. R. Hoagland for their kind help and advice.

<sup>2</sup> Here actual acidity means the same as hydrogen-ion concentration. Potential acidity means the changes in actual acidity obtained when acids or alkalies are added.



A humus-rich soil was put into four different beakers. One was covered with a glass and kept in the dark and at constant temperature; one was dried at room temperature (varying between 15° and 20°C.); one was dried at 100°C. and one at 150°C. After 14 days, the titration curves were made. Results are shown in table 1. From this it is seen that within the experimental error the results are quite congruent and the different treatment did not influence the acidity of the soil.

TABLE 1  
*The influence of drying on soil acidity*

KIND OF SOIL		TREATED WITH 0.1 N H <sub>2</sub> SO <sub>4</sub>					TREATED WITH 0.1 N NaOH				
A. Natural moist soil.....	cc.	2.50*	1.25	0.50	0.25	0.00	0.13	0.26	0.65	1.2	
	pH	4.3	5.2	6.2	7.0	7.2	7.3	7.3	7.4	8.0	
B. Air dried 15-20°C.....	cc.	2.62	1.51	0.52	0.26	0.00	0.13	0.27	0.67	1.33	
	pH	4.0	4.8	6.3	7.0	7.2	7.2	7.3	7.4	8.0	
C. Steam dried 100°.....	cc.	2.60	1.30	0.52	0.26	0.00	0.13	0.27	0.66	1.33	
	pH	4.1	5.3	6.3	7.0	7.2	7.3	7.3	7.4	8.0	
D. Heat dried 150°.....	cc.	2.50	1.25	0.50	0.25	0.00	0.13	0.26	0.64	1.27	
	pH	4.3	5.3	6.3	7.0	7.2	7.3	7.3	7.4	8.0	

\* In this, as well as tables 2 and 5-9, figures in italics show the amount of acid or alkali which has been added to the soil while the regular type shows the resulting reaction.

TABLE 2  
*The influence of different acids and alkalies on soil reaction*

ACID ADDED		TREATED WITH 0.1 N ACID				ALKALI ADDED		TREATED WITH 0.1 N ALKALI			
A. H <sub>2</sub> SO <sub>4</sub> .....	cc.	2.42	1.21	0.48	0.24	NaOH	cc.	0.00	0.12	0.25	0.61
	pH	3.1	4.1	5.0	6.2		pH	7.0	7.4	7.8	8.4
B. HCl.....	cc.	0.43	0.22	0.11	0.05	KOH	cc.	0.00	0.04	0.08	0.17
	pH	5.7	6.3	6.6	6.8		pH	7.0	7.4	7.6	8.0
C. HNO <sub>3</sub> .....	cc.	0.32	0.16	0.08	0.05	H <sub>4</sub> NOH	cc.	0.00	0.05	0.08	0.16
	pH	0.9	6.3	6.7	6.9		pH	7.0	7.2	7.5	7.8
D. CH <sub>3</sub> COOH...	cc.	0.35	0.18	0.09	0.05	Ba(OH) <sub>2</sub>	cc.	0.00	0.05	0.06	0.20
	pH	5.0	5.5	5.9	6.9		pH	7.0	7.4	7.6	8.0
After 3 days.....	pH	(5.6)		(6.0)			pH				

A short storage, therefore, as for transportation etc., does not interfere with the work, but one must be very careful with soils stored for a long time.<sup>3</sup>

Another objection is that one may obtain different results when using different acids or alkalies. In order to control this the titrations were made in

<sup>3</sup> In the case of the Java or Egyptian soils, where stored soils also were employed in the work, tests with the fresh field soil gave the same results as the stored ones.

four series, using  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ,  $\text{HNO}_3$  and  $\text{CH}_3\text{COOH}$ , as acids, and  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{NH}_4\text{OH}$  and  $\text{Ba}(\text{OH})_2$  for the alkalies. The results of these tests are given in table 2, which shows that within the limits of experimental error, equivalent amounts of acid or alkali caused equal changes except in the case of acetic acid which gave a higher acidity in the filtrate. But when the soil is left in contact with the acetic acid for a period of three days, the same results are obtained because of the low dissociation of the acetic acid and thus lower rate of action.

Before discussing the importance of the potential acidity, a short review must be given of the influence of hydrogen-ion concentration on most cultivated plants.

When the pH value is over 9 or under 4, growth is inhibited so that only a few species are able to grow there without being severely injured.

Such results were obtained in culture experiments by Hoagland (10) and others (13). As all these workers have made their experiments with either solution or sand cultures and as the conditions in these media probably are not quite natural, the author undertook a similar work with soil.

The soil employed is garden soil from Java (table 7). Eight pots were filled with this soil and they were treated with different amounts of acid and alkali so that a series of soils was obtained whose pH values were whole numbers and ranged from 3 to 10. Table 3 shows the effect of this treatment on germination, stand after 2 months, average leaf surface after 14 days and 2 months, and the total leaf surface after 2 months. These results show a close resemblance to those obtained either in sand or in water cultures. It is evident that the optimum hydrogen-ion concentration for all plants investigated lies within a wide range.

Within this optimum range, we find a mass of irregularities in the growth of plants which depend upon the influence of the actual acidity.

The bacterial flora (7) of the soil plays a very great rôle in the nutrition balance and life of higher plants. So, for instance, we have the different nitrifying bacteria working in different pH zones.

Some of the plant pathogenes<sup>4</sup> spend a part of their life cycle in the soil and are dependent on the hydrogen-ion concentration of the substrata; others are not, as is easily seen from table 4.

Probably the fauna of the soil also is strongly influenced by this factor as has been shown for earthworms (2).

The solubility of different salts is also dependent on the degree of acidity of the soil solution. For instance, iron phosphate and aluminum phosphate are precipitated at a pH value of 3 to 5. The same thing happens with other phosphates and calcium and magnesium salts, as is seen from the titrations by Hildebrand (9). In the case of aluminum salts a large amount of these in solution may cause a poisoning of plants, as is shown for rye and rice.

<sup>4</sup> The strains were kindly furnished by Prof. Horne, Univ. of Cal.

TABLE 3  
*The influence of soil acidity on plant growth*

SOIL REACTION	RATE OF GERMINATION	GERMINATION	LIVE PLANTS AFTER 2 MONTHS	AVERAGE LEAF SURFACE		TOTAL RELATIVE LEAF SURFACE AFTER 2 MONTHS
				14 days	2 months	
Bersim						
<i>pH</i>		<i>per cent</i>	<i>per cent</i>			
3	0.06	15	0	0	0	0
4	0.20	47	25	1.7	2.8	0.35
5	0.20	60	51	2.9	7.2	2.2
6	0.32	62	55	4.8	4.7	1.6
7	0.42	75	78	6.8	7.1	4.2
8	0.47	82	71	8.3	11.2	6.5
9	0.66	100	73	8.5	6.6	4.9
10	0.25	57	50	7.6	2.7	0.75
Barley						
3	0.13	65	72	21	39	18.3
4	0.23	95	71	27	36	24.1
5	0.18	97	66	29	53	33.4
6	0.29	95	100	29	63	59.8
7	0.25	100	90	30	67	60.3
8	0.31	97	74	34	65	46.8
9	0.31	100	93	32	80	74.4
10	0.26	100	54	30	38	20.5
Corn						
3	0.10	67	100	24	41	31.6
4	0.15	95	100	28	65	61.7
5	0.16	95	98	26	56	52.0
6	0.16	93	98	33	79	71.0
7	0.24	100	98	31	53	51.9
8	0.23	95	100	40	56	53.2
9	0.24	100	100	44	58	58.0
10	0.25	100	98	54	67	65.7
Cotton						
3	0.07	50	57	22	17	4.6
4	0.14	62	86	41	67	34.8
5	0.20	72	91	82	68	44.2
6	0.18	82	94	83	75	56.2
7	0.23	82	88	82	71	51.1
8	0.23	85	98	74	50	41.5
9	0.19	75	90	101	79	53.6
10	0.18	82	76	4	24	14.9

TABLE 3—Continued

SOIL REACTION	RATE OF GERMINATION	GERMINATION	LIVE PLANTS AFTER 2 MONTHS	AVERAGE LEAF SURFACE		TOTAL RELATIVE LEAF SURFACE AFTER 2 MONTHS
				14 days	2 months	
Wheat						
<i>pH</i>		<i>per cent</i>	<i>per cent</i>			
3	0.05	17	100	11	26	3.4
4	0.11	37	87	12	24	7.6
5	0.24	52	94	33	63	30.5
6	0.28	55	100	28	53	29.0
7	0.28	72	91	25	50	32.8
8	0.29	72	88	47	80	50.4
9	0.35	70	70	50	86	41.0
10	0.17	42	100	7	27	11.0

When working with different tropical and subtropical soils the author found a very good correlation in some cases between the fertility of the soil and the titration curve. When the soils showed a strong buffer effect,<sup>5</sup> they were of good fertility; when they acted as weak buffers, their fertility was poor, (see tables 5-8).

Table 5 represent 16 tobacco soils from Sumatra. The rest are grouped around the four here given. Those acting as good buffers and more alkaline than pH 7 are resistant against the tobacco-wilt disease (*Slijmziekte*, *Bact. solanacearum*). The weak buffer soils, and those more acid than pH 7, however, are often devastated by this disease. In the weak buffer soils, the reaction is easily changed into the optimum field of bacterial growth.

The investigations of 20 rice soils (4) from Java are represented by two soils (in table 6), Soere and Rimboel. Here we find the same conditions as in the former case, probably we have to deal with a weakening of the rice plant and possibly with the effect of aluminum. Of great interest is that these two soils are from the same district and of the same origin, but afterwards

TABLE 4  
Influence of hydrogen-ion concentration on viability of plant pathogens

NAME OF ORGANISM	INDEX OF VIABILITY AT DIFFERENT SOIL REACTIONS						
	pH 4	pH 5	pH 6	pH 7	pH 8	pH 9	pH 10
<i>Bacterium citriputale</i> .....	0	2	8	10	10	10	5
<i>Botrytis cinerea</i> (potatoes).....		8	7	5	4	3	2
<i>Pythium</i> sp. (potatoes).....		10	10	10	10	5	10
<i>Sclerotium rolfsii</i> (Iris).....	8	8	9	9	10	10	10
<i>Polystictum versicolor</i> .....	0	10	10	10	10	6	6
<i>Bact. solanacearum</i> (tobacco).....	0	5	10	6	0		

<sup>5</sup> By buffer effect is meant the ability to take up acids or alkalies without or but slightly changing the actual acidity.

differentiated by several factors. In the same table we find the result of a titration of a humus-rich garden soil and of a volcanic ash, taken fresh and stored for two years. It may be of interest to compare this young soil with the relatively old Demak soils.

The titration curves of some Egyptian (1) soils are found in table 7. Of these the Damanhour soil is exceedingly unfertile, the Nile suspension and the

TABLE 5

*Effect of addition of acid or alkali upon the hydrogen-ion concentration of tobacco soils (Sumatra)*

SOIL		TREATED WITH 0.1 N H <sub>2</sub> SO <sub>4</sub>					TREATED WITH 0.1 N NaOH				
		cc.	pH								
Kaloean Penang Black, good....	cc.	2.80	1.40	0.56	0.28	0.00	0.29	0.58	1.46	2.92	
	pH	4.0	5.0	7.0	7.2	7.2	7.4	7.6	8.4	9.5	
Songei Mentjirim Black, bad...	cc.	2.49	1.25	0.50	0.25	0.00	0.26	0.52	1.30	2.59	
	pH	2.5	3.5	4.5	5.5	7.0	7.5	8.0	>8.0	>8.0	
Toentongan Black, good.....	cc.	2.55	1.28	0.51	0.26	0.00	0.27	0.53	1.33	2.66	
	pH	4.0	5.0	6.0	6.8	7.0	7.2	7.5	8.0	>8.0	
Toentongan Red, bad.....	cc.	2.41	1.20	0.42	0.24	0.00	0.25	0.50	1.25	2.50	
	pH	2.0	3.0	4.0	5.0	6.7	7.2	8.0	>8.0	>8.0	

> This sign indicates "more than."

TABLE 6

*Effect of addition of acid or alkali upon the hydrogen-ion concentration of Java soils*

SOIL		TREATED WITH 0.1 N HCl					TREATED WITH 0.1 N NaOH				
		cc.	pH								
Rimboelor Demak, good.....	cc.	2.33	1.17	0.47	0.23	0.00	0.14	0.27	0.68	1.37	
	pH	6.5	7.2	7.7	7.8	7.8	7.9	8.1	9.0	10.0	
Soere Demak, bad.....	cc.	2.44	1.22	0.49	0.24	0.00	0.14	0.28	0.71	1.42	
	pH	3.8	5.0	6.5	6.7	7.0	7.2	7.4	8.8	9.8	
Garden soil Buitenzorg, good .....	cc.	4.8	4.24	2.94	2.12	0.84	0.42	0.00	0.24	0.50	
	pH	4.5	6.5	6.8	7.0	7.2	7.3	7.3	7.6	7.9	
								1.24	1.68	2.48	
								8.8	9.5	11.0	
Volcanic ash Kediri.....	cc.	2.12	1.06	0.41	0.20	0.00	0.12				
	pH	2.6	3.5	4.0	4.5	7.0	9.5				

garden soil, however, are very fertile. In this case we see that the pH value of the Damanhour soil lies on the alkaline side of the growth limit. The sand is a soil type which is easily reclaimed, but also very easily destroyed by alkali. Also in these soils we see the same thing as in the case of the volcanic ash and the Demak soils. The Nile suspension has a comparatively weak buffer action when compared with the old garden soil and Damanhour soil.

Among the California soils the strongest buffer effect was shown by the garden soil.

The soils 1, 3 and 6 (used by Stewart (15)) are of the same soil type and show similar titration curves, whereas number 7 is of another type; here, however, 3 and 7 are bad and 1 and 6 good. In this case the pH value is at the neutral point and apparently the changes in reaction caused by the plants do not form any unfavorable conditions, whereas other factors, as the amounts of nutrients present are the chief factors of growth.

Of great interest are the soils from Ignacio near San Francisco. One of the samples, an extremely acid subsoil, probably represents the soil type before being worked and limed. The unlimed soil is thoroughly worked, but not limed and is now yielding a poor crop of beets; on the same field a part was limed resulting in an exceedingly good crop. The value of the soils is quite in

TABLE 7  
*Effect of addition of acid or alkali upon the hydrogen-ion concentration of Egyptian soils*

SOIL USED		TREATED WITH 0.1 N HCl			TREATED WITH 0.1 N NaOH				
Garden soil Giza, good.....	cc.	3.17	1.98	0.75	0.00	0.29	1.02	2.08	
	pH	7.2	7.4	7.5	7.6	8.0	9.5	11.0	
Damanhour, soil, bad.....	cc.	0.00	0.31	0.72	1.15	1.56	2.15	3.71	5.4
	pH	11.00	10.0	9.0	8.7	8.4	8.1	7.6	7.3
Nile Suspension, Cairo.....	cc.	1.77	0.93	0.11	0.44	0.20	0.00	0.23	0.47
	pH	3.0	6.5	7.0	7.2	7.4	7.4	7.5	7.8
Sand El-Munayer.....	cc.	0.29	0.00	0.20	0.32	0.76		1.25	1.94
	pH	4.0	7.0	7.4	7.8	11		9.2	10.5

accordance with what has been said above on the correspondence between titration curve and soil fertility.

From the tables one sees that there is a correlation between the buffer action and the fertility of the soil. If the actual acidity of a soil lies within certain limits the buffer action of the soil is of great importance, so that strong buffer action is a good property; weak, a bad property. This action, however, is an indirect one. All soils are in a developing phase. The vegetation plays a great rôle on the one hand through the decomposing plant debris and root excretions and on the other hand through substances formed by the decomposition such as carbonic acid, etc. In arid climates the soil is more influenced by the formation of alkaline substances.

If there is, for instance, an acidifying process going on in the soil we may look at the process as a sort of a titration with an acid. A certain amount of acid substances is given off by the plant and in some soils we see a strong change caused by this action, in others the change is perhaps scarcely visible. The latter soils are the strong buffers, the former, weak. In this way the soil

reaction of the weak buffer soils is more easily changed to a range which is in some way injurious to the plant, than in the case with those having a strong buffer effect. Then the question arises how to improve the buffer effect of soil.

TABLE 8  
*Effect of addition of acid or alkali upon the hydrogen-ion concentration of California soils*

SOIL USED		TREATED WITH 0.1 N H <sub>2</sub> SO <sub>4</sub>				TREATED WITH 0.1 N NaOH				
1A.....	cc.	2.42	1.21	0.48	0.24	0.00	0.12	0.25	0.61	1.22
	pH	3.1	4.1	5.0	6.2	7.0	7.4	7.8	8.4	9.3
1B.....	cc.	2.29	1.15	0.45	0.23	0.00	0.11	0.23	0.58	1.17
	pH	3.3	4.5	5.4	5.9	7.0	7.4	7.8	8.1	9.0
3A.....	cc.	2.60	1.30	0.52	0.26	0.00	0.13	0.27	0.67	1.33
	pH	3.0	4.3	5.1	6.0	7.0	7.4	8.2	9.0	10.0
3B.....	cc.	2.25	1.12	0.45	0.23	0.00	0.12	0.24	0.57	1.14
	pH	3.3	4.8	5.8	6.2	7.0	7.4	7.8	8.4	9.5
6A.....	cc.	2.61	1.30	0.52	0.26	0.00	0.12	0.27	0.66	1.32
	pH	2.9	4.4	5.6	6.2	7.0	7.6	8.1	9.0	10.5
6B.....	cc.	2.35	1.17	0.47	0.24	0.00	0.12	0.25	0.60	1.19
	pH	3.2	4.8	5.9	6.4	7.0	7.5	7.8	8.3	9.7
7A.....	cc.	2.34	1.17	0.47	0.23	0.00	0.12	0.23	0.59	1.19
	pH	1.7	2.8	4.4	5.4	6.7	7.0	7.9	8.7	9.0
7B.....	cc.	2.16	1.08	0.43	0.22	0.00	0.11	0.22	0.55	1.10
	pH	2.0	3.0	4.6	5.4	6.7	7.0	7.7	8.7	9.5
Garden soil.....	cc.	4.44	2.22	1.11	0.44	0.22	0.00	0.05	0.11	0.57
	pH	2.5	4.8	5.2	6.2	7.0	7.2	7.3	7.3	7.4
									1.13	4.52
									8.0	12.0
Ignacio Hard, Sub-soil.....	cc.	3.04	1.52	0.61	0.30	0.0	0.16	0.31	0.78	1.55
	pH	2.3	3.0	4.0	4.8	5.1	5.8	6.1	6.7	8.2
Ignacio, Soft Limed, good.....	cc.	2.15	1.08	0.43	0.22	0.00	0.11	0.23	0.55	1.10
	pH	3.0	4.3	5.2	6.3	6.9	7.4	7.7	8.0	8.4

The nutrient salts of the soil are of very little importance as buffers as can be seen from table 8 where all "B" soils are unplanted and therefore rich in salts, and the "A" soils have been cropped for six years and are therefore rather exhausted.<sup>6</sup> Liming only moves the reaction over towards the alkaline

<sup>6</sup> In table 9 the titration of a modified Hoagland's solution is given. This represents a good soil solution. It can be seen that the titratable acidity is very weak when compared with that of the soils.



side and does not increase the buffer effect to any appreciable extent (as seen from the limed Ignacio soil).

It seems, considering Javanese and California garden soils as compared with the mineral soils from the same districts<sup>7</sup> that good humus-manuring would improve the buffer curves in a relatively short time.

Another way is suggested by comparison of the old and new soils. Through weathering and decomposition the buffer effect is increased. This process can be accelerated by cultivation.

It seems as if it would be possible to ascertain the lime requirement of a soil by titration. By lime requirement, one means two things, partly the amount of lime required for "neutralizing" a soil and partly, in lime-poor soils, the amount required to fill the nutrition balance. The "neutralizing" lime only, is to be considered here.

TABLE 9

*Effect of addition of acid or alkali upon the hydrogen-ion concentration of modified Hoagland's solution*

	0.1 N HCl		0.1 N NaOH							
	0.03	0.01	0.00	0.08	0.22	0.57	0.77	0.88		
Cc. of acid or alkali added per gm. solution . . . . .	3	4	5	6	7	8	9	10		
Resulting reaction of modified Hoagland's solution.										

A review of the literature shows that many methods have been used to determine soil acidity. There are three different types of these methods. First, the titration method in which only one actual pH determination is made, namely, the end point of the titration. Some use phenolphthalein, and others, other indicators.

Another type is that in which only a qualitative test with an arbitrarily chosen method is made.

Christensen used a biological method in which the growth of *Azotobacter* was the indicator.

What is done in all these cases and what it is aimed to do is to change the reaction of the soil to a certain point. Why not do it by titration with a strong but diluted acid (or alkali) in order to get the reaction as quickly as possible and then locate the different points on the pH scale. By using this method the arbitrariness would be reduced to a minimum and one would obtain a universal and simple method for the determination of the lime requirement.

#### SUMMARY

The potential acidity of the soil or the buffer action is an important and nearly overlooked factor. It has been found that in some cases there is a good correlation between the type of titration curve and fertility. A strong buffer

<sup>7</sup> A good suggestion in this work would be to select a certain green manure crop of which the manure is as near neutral as possible in order to avoid too much liming.

action means a good soil, a weak one a bad or easily changed soil, provided the reaction of the soil lies within certain limits. Humus-manuring and cultivation are the two factors for increasing the buffer effect.

The titration of soils may be used for determination of the lime requirement.

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